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THE FUNDAMENTAL PROCESSES OF DYE CHEMISTRY

PLATE I.

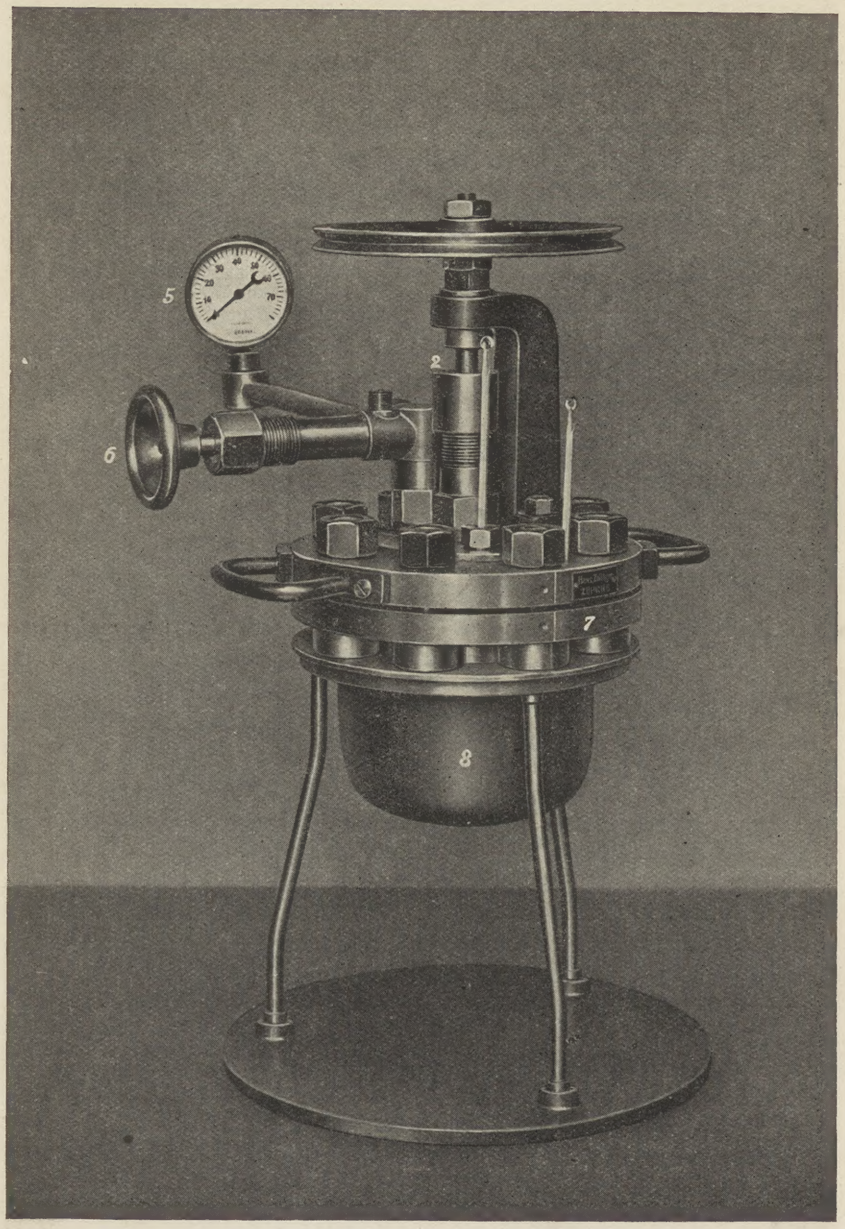

FIG. 1.—Laboratory autoclave fitted with stirring gear. (Constructed of cast-steel. Working pressure 60 atms. Capacity, 1 litre. Weight, 33 kg. Weight of oil-bath, 11 kg.)

[*Frontispiece.*

THE FUNDAMENTAL PROCESSES OF
DYE CHEMISTRY

BY

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RESEARCH CHEMIST WITH THE BRITISH DYESTUFFS CORPORATION,
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PREFACE TO THE ENGLISH EDITION

In preparing an English edition of Prof. Fierz-David's well-known work on the practical side of dye chemistry, advantage has been taken of the opportunity to correct one or two slight errors that had crept into the original Swiss edition, and to make an alteration to Plate XV. For the rest, the book remains practically unaltered.

In most cases the original weights and prices have been retained (in francs per kilo.), instead of trying to convert them into shillings per pound. It was felt that, as the figures referred usually to pre-war conditions in Switzerland, and having regard to the present unsettled state of the exchanges and of production costs, no good purpose would be served by attempting to give the English equivalents which, in any case, would in all probability only be misleading.

I wish to acknowledge, with much gratitude, the assistance rendered by my wife during the translation; and to Mr. C. Hollins my best thanks are due for his kindness in giving much valuable help in revising the manuscript and the proofs.

F. A. MASON.

1 [illegible]3

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INTRODUCTION

Although well aware of the existence of a large literature dealing with laboratory practice, I have written this book because there does not appear to exist a suitable introduction to the fundamental operations of dye chemistry.

Ignorance of elementary facts leads in practice to waste of time, which may be redeemed in part by suitable instruction ; nor should it be forgotten that many of the essential features of chemical craft may be learnt from books.

The manufacture of synthetic colours has attained to such importance that it seems desirable to familiarize the rising generation of chemical technologists with the methods of production of the more important intermediates. With this end in view, I have attempted a description of these methods in a manner which may be helpful even to those unfamiliar with technical operations.

Azo colours form the largest section of artificial dyes, and in consequence most attention has been devoted to the preparation of the necessary intermediates. As, however, many of these intermediates are also used in the synthesis of other classes of dyes, such as Indigo, Azines, Thiazines, Aniline Black, Sulphur colours, and Triphenyl-methane dyes, it may fairly be claimed that the field of synthetic colours in its essential features is covered by the present volume.

To complete the picture I have added recipes for a few dyes and included some general observations on the technique of dye manufacture. With only trifling exceptions the dyes dealt with can all be obtained from the intermediates described in the first portion, so that the student is enabled to obtain a clear view of the stages of development of a dye.

In this industry there are certain fundamental operations which are constantly repeated with slight but important modifications ; for this reason I have purposely given the first few recipes in as great detail as possible, and frequent references will be made to them later.

I have also attempted to describe the processes in such a way as to give, besides the laboratory details, a clear indication of the method of carrying out the process in the works. There would be no point whatever in giving either laboratory recipes or works recipes alone, as only by an acquaintanceship with both can the budding chemist get an insight into the technical side of the dye industry, since laboratory and works must be regarded as parts of an indivisible whole.

I wish also to emphasize the fact that any process which is successful in the laboratory will also succeed on the large scale when the necessary alterations for dealing with the larger quantities involved have been made; this may, indeed, be regarded as a fundamental principle by every technical chemist.

Lastly, I would observe that the use of too little material in technical laboratory experiments leads to inaccurate results. For this reason, it is the general practice to measure the laboratory charge in gram-molecules which, multiplied by a thousand, gives at once the scale for works practice.

Too much stress cannot be laid on the fact that the material of which the apparatus is constructed plays an important part in every process; for this reason every chemist should be quite clear in his own mind as to the suitability of various materials for different chemical processes, as by this means he will be able to avoid many an unwelcome breakdown.

Objection may be taken to the fact that the patent literature of the subject has been almost entirely neglected; this, however, has been done on purpose, as the beginner is as likely as not to be confused by numerous references. Those who desire information on patents will find all they require in the excellent collections of patents compiled by Friedlaender and by Winther. In these volumes a short summary is given for each class of dyes, including references to all the important work on the subject. In my opinion, it is far better for the beginner to get a good knowledge of the few facts that he will find in any reliable text-book of organic chemistry than to attempt to become acquainted with the confusing details of innumerable patents.

The recipes given in this book must, of course, only be regarded in the light of finger-posts, and they make no claim to be the best, for many paths lead to Rome. All the examples given, however, have been actually tested by the author, and in the majority of cases they have also been put through in the works, under his supervision, so that they may be regarded as being technically satisfactory.

H. E. F.

THE FUNDAMENTAL PROCESSES OF DYE CHEMISTRY

I. INTERMEDIATE PRODUCTS

General Considerations.

THE term Intermediate Products is applied, in the dye industry, to those substances obtained from organic products, whether aromatic or aliphatic, which are devoid of dye character. The most important raw materials are Benzene and its homologues, Naphthalene and Anthracene, and, to a lesser extent, certain aliphatic bodies such as Methyl and Ethyl alcohol, Acetic acid, and various other less important substances which are utilized chiefly for special brands of colours.

From these raw materials the intermediate products are obtained by means of certain comparatively simple chemical operations; the hydrocarbons which serve as the starting-point are obtained by the colour factories from the tar distilleries. In many cases it is found that the yields obtained can be increased almost up to the theoretical by paying scrupulous attention to all the conditions. For this reason, as was indicated in the Introduction, the recipes have been given in almost exaggerated detail, but every technical chemist will agree with me that a good recipe cannot be given too accurately, for quite slight errors may often cause very considerable variations in the final product.

It has further been found that the manufacture of the intermediate products is far more difficult than that of the finished colouring matters, and, in addition, the apparatus and machinery needed for the intermediates occupies a far greater space than that required for the actual dyes. The Anthraquinone dyes, however, form an exception to this generalization. With the exception of this last case it may be said that the ratio of the size of the installations and the number of workmen required for intermediates and dyes respectively is approximately as 3:1, or, in other words, a colour factory which has previously purchased its intermediates and now intends to make them itself must enlarge itself about fourfold.

Further, it is found that the apparatus used for the production of Intermediates is very rapidly destroyed by the chemicals used, which is hardly surprising when one considers that for the most part they have strong acids and alkalis to deal with. For these reasons, in a well-conducted factory, all the apparatus should be fully written off.

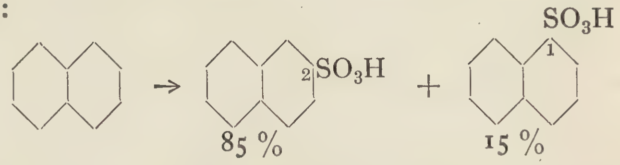
It may be pointed out at once that the arrangement of the Intermediate Products which has been selected in the first part of this book will hardly bear serious criticism from the purely scientific standpoint. I have, for instance, under the heading of Sulphonations included quite a number of other operations. This arbitrary choice, however, will be found to justify itself in the sequel, since it is obviously undesirable that a product such as Aminonaphthol-disulphonic-acid 1:8:3:6 (H-acid) should be dealt with under four different headings; any such attempt would obviously be contrary to the dictates both of convenience and of common sense.

For the rest, the Index will afford any further information in cases of doubt.

1. *SULPHONATIONS*

β-Naphthalene-monosulphonic Acid and β-Naphthol.

Reaction :



This product may be prepared by several different methods. If the β-monosulphonic acid is to serve for the preparation of β-Naphthol, the sulphuric acid must be completely utilized, as the product is so cheap that only the best process is capable of competing. (For further details, see β-Naphthol.) The method for preparing the Di- and Tri-sulphonic acids is given under H-acid.

The sulphonation of naphthalene at elevated temperatures (170° C.) leads to the formation of naphthalene β-sulphonic acid. A certain quantity of the alpha acid is always produced at the same time, amounting to about 15% at least, according to the results obtained by various experimenters. The researches of O. N. Witt[1] have shed a good deal of light, in certain directions, on the complex relationships involved. In actual practice, however, where it is necessary to obtain the highest possible yield of β-naphthol from the minimum possible quantity of sulphuric acid, Witt's process is hardly suitable.

---

[1] *Berichte*, 1915, p. 743.

The following quantities give satisfactory results :—

260 gms. Naphthalene = 2 mols.
280 gms. Sulphuric acid, 66° Bé. = 93 %.

260 gms. Naphth. 280 gms. H_2SO_4.

The naphthalene used must be perfectly pure, must have no unpleasant tarry odour, and should not discolour on heating in a test-tube with concentrated sulphuric acid. The German tar-distilleries used to deliver naphthalene which met every requirement.

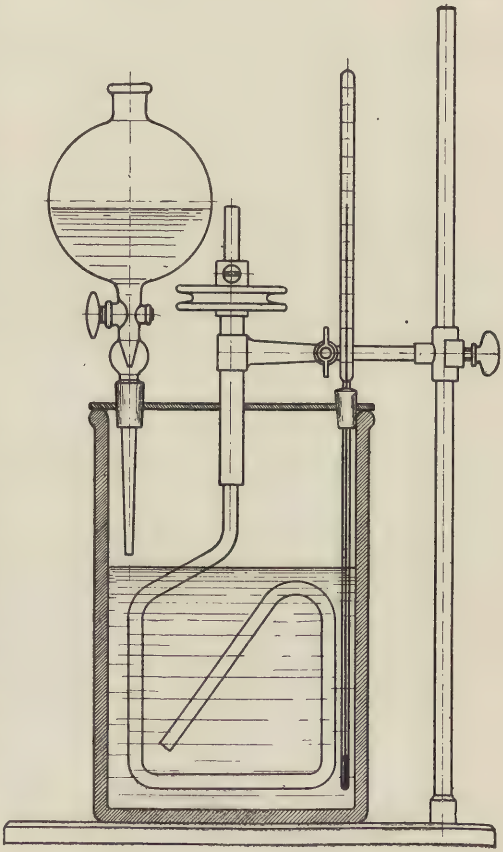


Fig. 2.—Sulphonating pot for naphthale sulphonic acids.

Laboratory Apparatus (see Fig. 2).—This consists of a sheet-iron, or, better, a cast-iron (or porcelain or glass), beaker of about 11 cm. diameter and some 20 cm. high. A well-fitting cover made of sheet lead is provided, through which pass the stirrer, thermometer, and tube for the addition of the acid. The type of stirrer shown in the figure has been found very suitable; it can be readily made from glass rod, and may be used for all purposes where the mechanical strain is not too great. In general, however, iron is to be preferred. The sleeve carrying the stirrer is best made of copper, as both glass and iron run very freely on copper on a small scale, and it does not tend to "corrode" the stirrer so much. The driving pulley may be made of bronze, as this metal also runs very well on copper, especially if vaseline be used as a lubricant. The thermometer should have the scale on the upper portion, and should dip down as far as possible. Further, I may remark that in all cases where it is necessary to watch the addition of any liquid very carefully, a dropping funnel with a drop-counter (as shown) should be used. The pot must stand on a good substantial retort-stand, and the copper "sleeve" must be fixed with a strong clamp. The thermometer and the dropping funnel must also be fixed firmly and in such a manner that the stirrer cannot come in contact with either.

The weighed quantity of naphthalene is heated directly in the beaker to 165°, with continuous stirring. As soon as this temperature has been attained the sulphuric acid is allowed to run in during half an hour, the gas being so regulated that the temperature remains constant between 163° and 168°. The dropping funnel is then removed, its place being taken by a bent glass tube, which is fitted tightly to the cover by means of cork or asbestos paper. Water and naphthalene distil off through this tube during the course of the sulphonation. The mixture of naphthalene and sulphuric acid is now kept at 165° for an hour with continuous stirring, then for one hour at 167°, then at 170° for an hour, and, finally, for an hour at 173°. During this operation about 30 gms. water and 25 gms. naphthalene can be collected in the receiver. An appreciable amount of naphthalene also condenses by degrees on the cover of the vessel, but may be disregarded. The flame is then removed, and the apparatus dismantled. The resultant mixture contains, besides naphthalene sulphonic acid, a certain quantity of sulphones, a little free sulphuric acid, and some disulphonic acids, together with some resinous matters. The product should be colourless. 1·8 l. Water. It is then poured into 1·8 litres water. The further working up may be carried out in numerous ways, and many different methods are adopted in the various factories. Some partially neutralize and then salt out the naphthalene sulphonic acids. Others prefer to "lime out" first, then converting into the sodium salt by means of Glauber salt, after which the calcium sulphate is filtered off, the residue being evaporated down and then worked up further. The simplest method is to salt out directly without attempting to neutralize at all, but this has the disadvantage that the strongly acid filtrate rapidly destroys both filter-cloths and filter-presses, and also that on drying the sodium salt of the monosulphonic acid the entire vicinity is polluted by the great quantities of hydrochloric acid which are given off.

The solution of the free sulphonic acids is now partially neutralized by sprinkling in 60 gms. of soda, with good stirring. 360 gms. of common salt are then added slowly; after a short time the liquid begins to solidify to a mass of large lumps which make further stirring very difficult. Nevertheless, the stirring must be continued until the mass again appears to be completely homogeneous, as only by this means can one ensure that the salt will be completely dissolved and that a precipitate will be obtained which will filter well. The actual amount of stirring required depends upon the speed of rotation of the stirrer, but in any case at least 6 hours will be requisite, otherwise the separation will be incomplete. The precipitate is then introduced into a suction filter provided with a cotton filter cloth and thoroughly pressed down. After removal from the filter the product is placed in a strong, moistened cotton cloth and pressed, gently at first, and then more energetically, in a screw press. The pressing should take at least 2 hours, otherwise too much mother-liquor remains in the cake. The hard mass is then ground up and dried completely at 100–120° C.

60 gms. soda.
360 gms, NaCl.

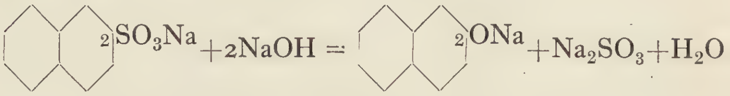
The yield of "β-salt" is about 165 %, *calculated on the weight of naphthalene taken, which corresponds in this case to a yield of* 400–420 *gms.*

The mother-liquors can be worked up for Glauber's salt; it contains a little α-acid, together with resins and traces of β-acid.

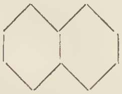
The Melt of the sodium naphthalene sulphonate is one of the most important operations of applied organic chemistry. When one considers the very low price obtained for Naphthol it is hardly surprising that only quite a few factories manufacture this product. Cheap raw materials, such as coal, soda, and sulphuric acid, are, of course, essential. The waste heat from the melt pots must be utilized for drying the sodium salt and the Glauber's salt and sulphite produced as by-products, or the sulphurous acid must be recovered. A naphthol works that does not completely recover all its by-products is incapable of competing in the open market.

Fusion Pot (see Fig. 3).—On the laboratory scale the pot is best made of copper which, on account of its good conductivity, leads to a considerable saving of gas, and is therefore very cheap to work with. The same remarks that were made as to the moving parts of the apparatus in the case of the sulphonating vessel apply in the present case (p. 5). The high melting-point of the naphthol renders it necessary for the stirrer to scrape the entire surface of the vessel (see figure). The thermometer dips into a narrow copper tube which is brazed together at the bottom and filled with lubricating oil to a sufficient extent to ensure that at least 10 cm. of the thermometer is covered. Another good plan is to have the thermometer fitted into the hollow spindle of the stirrer.

Reaction :



(Side reaction :



$+Na_2SO_4$)

In order to ensure that the caustic soda and the sodium salt shall fuse together readily it is necessary that the latter be as finely powdered as possible. In the laboratory this is most conveniently effected by grinding the coarse salt in a powerful coffee mill.

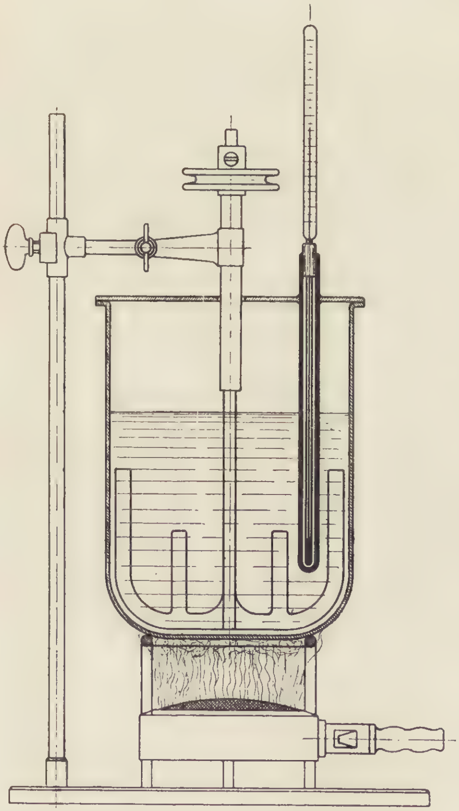


FIG. 3.—Fusion pot for β-naphthol.

200 gms. NaOH.

60 c.cs. H_2O.

The fusion pot is now placed directly on a small Fletcher burner and is charged with 200 gms. solid caustic soda, free from chlorate, in coarse lumps and 60 c.cs. water. If the caustic contains chlorate the yield will be diminished, and there is also very great risk of explosion. The caustic soda is melted to a clear liquid with the aid of a full flame and the temperature raised by degrees to 270° ; the foaming which occurs during the heating ceases at that temperature. The powdered sodium salt is now added continuously, a spoonful at a time with stirring, the temperature being

300 gms. β-salt.

allowed to rise slowly to 290°. The dry sodium salt will be seen to disappear slowly, giving place to the dark, mobile, and glistening sodium naphtholate. Owing to the fluid character of the naphtholate it is now possible to add considerably more sodium salt than is given in most recipes. In the laboratory it is quite easy to work with $1\frac{1}{2}$ parts of sodium salt for each part of caustic soda used. On the works scale, given suitably constructed apparatus and adequate heating, *e.g.* with generator gas, it is possible to add 2·8 parts of salt to each part of caustic without any danger of burning, or of the mass becoming too thick. About half the β-salt (150 gms.) should have been added by the time the temperature has reached 290°. The temperature is now raised cautiously to 300°, then, when three-quarters of the salt (225 gms.) have been added, to 305°, and, finally, when it has all been added, to 318°. On no account must this latter temperature be exceeded. The melt attains by degrees a gritty consistency due to the separation of sodium sulphite, and the caustic soda is slowly displaced by the naphtholate. The whole melt is now kept for 15 minutes at 318° with continuous stirring, taking care that no overheating occurs. The complete process, from the time of the first addition, should occupy about one hour ; if the salt be added too quickly some charring will occur with inevitable lessening of the yield.

The contents of the fusion pot are now poured on to a tin tray. As soon as it is cold the product is broken up and returned to the pot, together with $\frac{1}{2}$ litre of water. On warming gently a considerable portion goes into solution, but a crust of sodium sulphite always remains behind ; the solution is therefore poured off and fresh water added until the entire melt is in solution. It should not be necessary to use more than 2 litres for this purpose. The solutions are then mixed and heated to boiling over a Fletcher burner and treated with 50 % sulphuric acid until practically no reaction is given with thiazole paper ; after cooling somewhat the liquid is sucked into a pre-warmed flask through a large porcelain filter-funnel (" Nutsche "). The volume of the neutral and filtered solution should be about 3 litres, and its colour not more than faint yellow.

This solution is now heated to boiling, and, whilst stirring well, sufficient 50 % sulphuric acid is added until litmus paper is strongly reddened. There will be no odour of sulphurous acid, as β-naphthol is insoluble in neutral sodium sulphite in presence of a little bisulphite, and therefore separates out, at first as an oil, which immediately solidifies. The precipitated substance may be filtered off after an hour or so without losing more than a trace of naphthol, using a cotton filter-cloth, and washing the product carefully with water. Before distillation the naphthol should be dried at a low temperature either in a vacuum drying chest or in a warm room ; if it is heated too much it melts and sublimes.

The yield of dried crude naphthol from 300 *gms. β-salt is about* 150 *gms.* (93 % *pure*), *and of distilled product* 135 *gms. M.p.* 122°.

The crude product is quite adequate for most purposes, but for sale it must be carefully purified owing to the very high standard required. At the present day vacuum distillation only is made use of (*q.v.*), but for many years the B.A.S.F., for example, distilled all their naphthol with super-heated steam in order to get a really first-class product. (The important method of steam-distillation will be discussed later.)

Notes on Works Technique and Practice.—The sulphonation of naphthalene is always carried out on the large scale in huge cast-iron vessels holding 1000 to 3000 litres. They are heated either with direct (generator) gas heating, or by means of a steam jacket (double-bottom), which must be capable of withstanding at least 6 atmospheres in order to attain the requisite temperature of 174°.

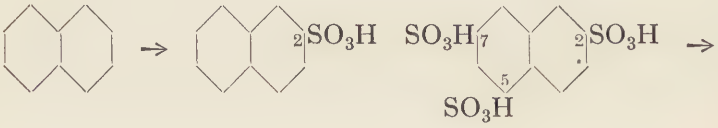
(See Plate II.)

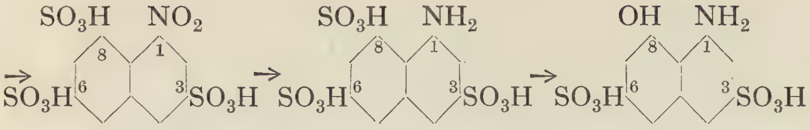
The precipitation of the naphthalene salt is effected in wooden vats (Plate VII.). The filtration is done in wooden presses, and the salt wrapped in hair cloths, after which it is pressed in hydraulic presses at about 250 atmospheres. Hydraulic accumulators are not to be recommended for this purpose, as the rapid increase in pressure invariably bursts the cloths. Small pumps, such as that shown in Plate III., however, are very suitable for the purpose, as they cause a gradual increase in pressure, and cut out automatically as soon as the maximum has been reached.

The melt is carried out in flat cast-iron pans with a plough stirrer, the heating being either by means of coal or, better, by generator-gas, the waste heat, as already mentioned, being utilized for drying the naphthalene salt in drying ovens.

Naphthylaminetrisulphonic acid 1:8:3:6 and Aminonaphtholdisulphonic acid 1:8:3:6 (H-acid).

Reaction :





In order to carry the sulphonation beyond the beta-sulphonic acid stage it is necessary to make use of a considerable excess of sulphuric acid; the acids so obtained are then usually cooled and nitrated. If too little sulphuric be used thick and viscous products are obtained after the sulphonation, which render stirring impossible. The excess of sulphuric acid acts as a diluent, but may be reduced somewhat on a works scale as more powerful stirring appliances are available.

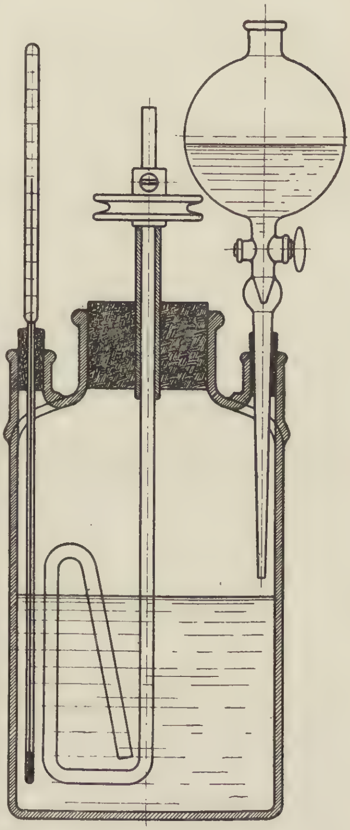


Fig. 4.—Autogenously welded sulphonating pot for use with oleum. Suitable also for the preparation of aniline, etc.

The apparatus required is the same as that described for the preparation of naphthalene sulphonic acid, or as shown in Fig. 4. It consists of an iron vessel which has, besides the large central opening, two smaller necks through which the thermometer and funnel are inserted. The trouble with sulphur trioxide vapours is almost completely avoided in this manner, and, in addition, the vessel can never crack when placed in cold water, which would, of course, be very dangerous when using oleum.

256 gms. Naphthalene.

We start with 2 gram-molecules of naphthalene, which, as in the sulphonation for β-naphthol, is heated to 165°. For the sulphonation, however, 100 % sulphuric acid is used, not 93 %, so as to avoid wasting any sulphuric anhydride afterwards by combination with the water.

If we used, for example, instead of the 280-gm. monohydrate the same weight of 93 % acid, then we should by this means be introducing 18 gms. (=1 mol.) water into the reaction mixture at the very beginning, which alone, in order to obtain any trisulphonic acid, would require the addition of 1 mol. SO_3, or 200 gms. of 40 % fuming acid, which would thus be completely wasted.

280 gms. H_2SO_4 (100 %).

280 Gms. of monohydrate are added cautiously drop by drop to the naphthalene melt, which is kept vigorously stirred. It is inadvisable to work too quickly, as otherwise local cooling may occur, which favours the formation of the α-acid. Under the conditions given the addition should occupy about half an hour; the mixture becomes very hot, differing thus from the sulphonation, for which reason only very slight heating is required, or none at all. The cooling due to radiation compensates almost exactly for the heating due to the chemical reaction. When the mixture is complete, the product is kept for a further hour at 165°, and is then cooled down by placing the pot in ice-water until the contents show a temperature of 75°. It is inadvisable to cool below this temperature, as otherwise the contents are liable to solidify, and can then no longer be stirred. The further sulphonation with fuming sulphuric acid leads to a whole series of isomers which are only partially known. By keeping exactly, however, to certain definite conditions, it is possible so to favour the formation of the 1:3:6 acid, that approximately 60 % of the desired compound may be obtained. In order to obtain the trisulphonic acid of naphthalene, at least so much sulphuric anhydride must be used that no water will occur in the equation at the end of the reaction. In other words, at the end of the process only monohydrate or a very weak fuming sulphuric acid should be present in the product besides the trisulphonic acid. If this necessary minimum quantity of SO_3 is not used, it will be impossible to convert all the naphthalene into the trisulphonated derivative, no matter how long it is heated, and the yield will be diminished by an amount equal to four times the quantity of the insufficiently sulphonated substance.

This affords an example of a phenomenon which is frequently observed in applied organic chemistry:—

Slight variations from the optimum conditions will cause losses which, apparently, are quite out of proportion to the error which has been made.

No harm, however; will be caused by an excess of sulphuric anhydride, so long as this is kept within reasonable limits; in recognition of this fact an excess of about 10–15 % of SO_3 is taken. Commercial fuming sulphuric acid contains almost invariably too little anhydride, owing to the absorption of a little water whilst transferring to smaller vessels. As a simple calculation shows, however, very slight quantities of water reduce the SO_3 content to quite an extraordinary degree. The oleum which is used in the

PLATE II.

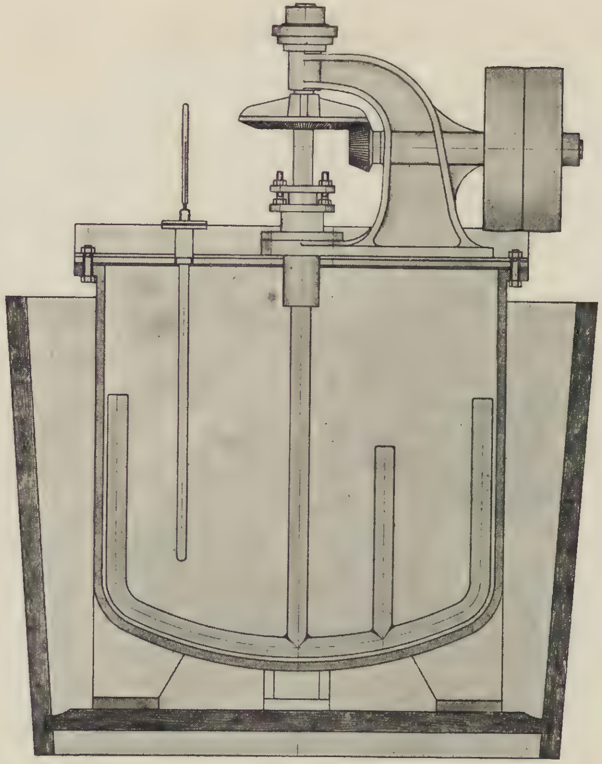


FIG. 6.—Sulphonating and nitrating pot in wooden tub for heating or cooling.

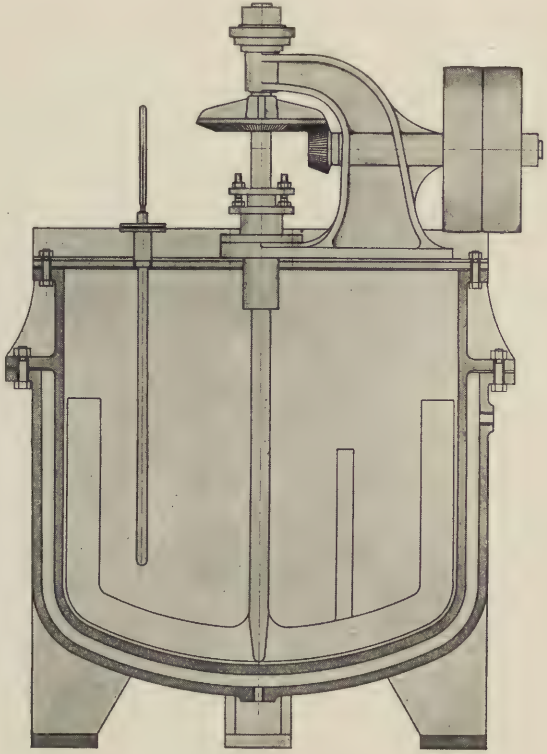


FIG. 7.—Sulphonating and nitrating pot with steam-jacket.

works has a much more constant composition, as it is less easy for water to be absorbed by the large quantities of acid dealt with. To a great extent the concentration of the oleum used depends upon the personal preferences of the works chemist; sulphuric acid containing anything from 30–60 % SO_3 may be used without hesitation, but the latter strength (60 %) is recommended, as it remains liquid at lower temperatures and does not require any troublesome heating.

It is very important that the temperature at which naphthalene-monosulphonic acid and sulphur trioxide are mixed should be as low as possible, or else losses are caused owing to SO_3 distilling off, and to charring. As soon as the temperature of the monosulphonic acid has fallen to 75°, 120 gms. of monohydrate are mixed with the product in order to prevent the contents of the vessel from solidifying on further cooling. The mixture is allowed to cool with continuous stirring to 50°, and the cautious addition of the oleum is then begun. At first the mixture heats up very strongly, for which reason it is necessary to start very slowly. As soon as the water produced in the reaction has been used up, it becomes possible to work more quickly, and, finally, the remainder of the acid may be run in during the course of a few minutes. The addition of the oleum will occupy in the laboratory from half to one and a half hours, according to the amount of cooling. The mixture is now heated to 165°, and kept at this temperature for 6 hours with slow, continuous stirring. This length of time must be strictly adhered to, although, as may easily be observed, the odour of SO_3 will have disappeared after half an hour. During the slow heating, however, transformations take place which have been little investigated, but which, without any doubt, lead towards the formation of the desired trisulphonic acid.

120 gms. H_2SO_4 (100 %).

900 gms. SO_3 (60%).

We now convert the trisulphonic acid so obtained, without isolating it, into the nitro-trisulphonic acid 1:3:6:8. The nitration of the mixture of the numerous isomers leads, of course, to the formation of quite a number of nitrosulphonic acids which must be regarded as so much ballast. Besides the isomers, however, oxidation products are also formed which affect the yield. In the laboratory the nitration is done in the same vessel in which the sulphonation is carried out, placing it for this purpose in ice-water. For two molecules naphthalene, two molecules nitric acid are required, preferably as 60 % HNO_3 (40° Bé.). This quantity of acid is added slowly through the dropping funnel, temperature about 15–20°. In the laboratory the nitration should occupy about 3 hours. After all the nitric acid has been run in, the mixture is allowed to stand at 25° for at least 10 hours, and is then poured into 3 litres of water; volumes of nitrous fumes are given off and the aqueous solution heats up to 70–80°.

There are a number of methods for isolating the nitro-naphthalene trisulphonic acid or the naphthylamine trisulphonic acid. Most of these, however, are devoid of technical interest owing to various disadvantages. It would appear to be a simple matter to isolate the nitro-naphthalene trisulphonic acid, as about 95 % of it separates out in the form of its acid sodium salt on the addition of common salt; after standing for some time this is filtered off, the resultant cakes are pressed by hydraulic means, dissolved in soda, and then reduced in faintly acid solution. Although this process appears quite simple at first sight, and offers the attraction of recovering the sulphuric acid by avoiding the liming-out process, it is, nevertheless, impossible to carry out owing to the almost insuperable difficulties involved in dealing with the acid solutions. All the apparatus, filter-cloths, etc., are rapidly destroyed by the 24 % hydrochloric acid, repairs use up a great deal of material, and good workmen refuse after a time to take charge of such unpleasant operations. In addition, quite slight alterations in the composition of the nitrating liquid may prevent the complete separation of the nitro acid. In the laboratory, however, this method is quite suitable for obtaining quickly a supply of pure H-acid.

Again, the original process of D. R. P. 56058 is not a practical one, as, according to this method, the entire solution of the nitro-product is reduced with iron. The large quantities of gypsum mixed with the still larger quantities of iron hydroxide which are formed on liming the entire liquid make this process very unprofitable; further, the huge quantities of water which would have to be evaporated off would alone suffice to settle its fate.

The best and most generally used process consists in first removing the excess of sulphuric acid by means of lime, and then reducing the sodium salt. The first advantage in so doing is that the alkaline-earth or alkali salts of any aromatic nitrosulphonic acid can be reduced in neutral solution; this is the same principle that has been made use of for a very long time for the preparation of aniline. During the neutral, or more accurately faintly acid reduction of the product in question, only quite slight quantities of iron go into solution, and the chief amount of the iron oxide appears in the form of the black ferroso-ferric oxide which, owing to its small bulk and excellent filtering qualities, shows obvious advantages over the hydrated iron oxide. The quality of the iron used is a very important matter, and failures during the neutral reduction are, in most cases, due to the use of poor quality iron; only grey cast-iron is suitable, and neither raw iron, steel, nor wrought iron should be used, as under the conditions which we have chosen, they exert no reducing action.

The removal of the excess of sulphuric acid may be effected by the use either of slaked lime or of pure, finely powdered chalk. It will be found that calcium carbonate is the most convenient, as it gives a much more compact and easily filterable gypsum. It has, however, the disadvantage that the carbon dioxide evolved may lead to frothing-over, but this can be avoided by an experienced workman. It is, of course, possible to recover the carbonic acid, but a compressing plant for carbon dioxide presupposes, in this case, a very well-organized factory which is not afraid of expending money on plant and can, in addition, make use of the gas for the production of salicylic or *o*-cresotinic acids.

The decomposition of the sulphonic acids is always carried out in conjunction with the conversion into the sodium salt; this is done by the addition of the calculated quantity of Glauber salt to the liquor which is to be limed. The resulting calcium salts of the sulphonic acids immediately react with the Glauber salt to give the sodium salt and gypsum. Factories which make formic acid have such cheap Glauber salt at their disposal that the saving is very considerable in comparison with soda. Three molecules (450 gms.) of crude anhydrous Glauber salt are first added to the sulphuric acid solution, and then finely powdered limestone is added by degrees, with good stirring. About the same weight of limestone is required as of the sulphuric acid, since both compounds have almost the same molecular weight. We require, therefore, about 1300 gms. limestone or chalk, corresponding to the 1300 gms. of sulphuric acid (oleum and monohydrate) which was taken.

450 gms. Glauber salt.

1300 gms. Limestone.

The vessel in which this is carried out is a large glass cylinder holding 5 litres, provided with a glass stirrer of similar shape to that used for the sulphonation. It is advisable to calibrate the vessel beforehand, and to paint on it a scale showing every half-litre; small trifles like this facilitate the work in the laboratory to a surprising degree, besides training the eye (Fig. 21).

The addition of the carbonate (lime-paste may also be used) must be made very cautiously; any excess must be avoided, particularly where slaked lime is used, as the nitro acids are, in general, sensitive to alkali. As soon as the mineral acid has been used up, the pale yellow colour of the paste changes to a strong yellow, thus indicating the end of the liming; the gypsum renders the mass so thick that it becomes extremely difficult to stir, but on further stirring the paste becomes thinner, so that there is no difficulty in filtering. For this large quantity of gypsum, about three large porcelain suction filters are required, using either paper or cotton filters. The gypsum should be kneaded with a big spatula, and will then be found to shrink together to a remarkable degree. After the precipitate has been well pressed down, it is washed out carefully with cold water, filling up all the cracks at once. It is quite easy, with thorough washing, to keep the total volume of liquid below 5 litres; in passing it may be noted that there is no point in carrying the washing process too far. The colour of the sodium salts of the nitro acids is so intense that at least 10 litres of washing water are required before a colourless filtrate is obtained. In cases where uncertainty is felt as to this process, it is best to wash out with about a litre of water, tip the precipitate again into the stirring vessel, and then to paste up the gypsum carefully with 3 litres of water; it is then filtered off again as described above, and washed out with a little water. Any rise of temperature above 50° must be avoided as far as possible, particularly when the liming out is done with slaked lime.

It is not possible to evaporate down the solution of the sodium salts of the various nitro-naphthalene trisulphonic acids, as these are easily decomposed. It therefore becomes necessary to reduce the whole solution, which requires, of course, very large reduction vessels.

The reduction of the nitro-naphthalene trisulphonic acid is such a typical example of this kind of reaction that it will be as well to describe it in some detail. It must be carried out at the boiling-point, as in all reductions of this type, or else azoxy compounds are formed which cannot be reduced to the amino compound, or only with great difficulty.

The apparatus required for this reaction consists of a capacious sheet-iron pot, holding at least 4 litres, and provided with a propeller stirrer (which can be easily made by any tinsmith), by means of which it is possible to keep the iron used in the reaction in continuous motion. The propeller blades soon get used up, so that they are best fixed to the end of the stirring rod by simple riveting. (See Fig. 5, p. 17). If no propeller agitator is available, a stirrer of the form used for the sulphonation of naphthalene to the β-acid may be employed if due care be taken. The important point to notice is that the iron powder must not lie at the bottom of the pot, but must be kept swirling round. The iron pot should be made from lead-lined iron plate to prevent it from rusting too quickly; further, to prevent it from leaking, it should be lapped.

300 gms. Iron.
20 c.c. 40 % Acetic acid.
½ l. Water.

The pot is placed on a ring burner and filled with 300 gms. sifted iron turnings and about half a litre of water. To these are added 20 c.c. of acetic acid (40 %), and the mixture is then boiled up well with good stirring. In technical language the iron becomes "etched." Oxide, oil, and so on are removed in this manner, and the iron converted into the desired active form. Meanwhile, the solution of the nitronaphthalene trisulphonic acid is made just acid to Congo with dilute sulphuric acid. It is also possible to use the much cheaper sulphuric acid in place of the expensive acetic acid for "etching" the iron, but the yield of naphthylamine trisulphonic acid is affected unfavourably by it, being reduced by 10–20 %. It is therefore strongly desirable to reduce in acetic acid solution. In the case of other amino acids, such as Cleve and naphthylamine sulphonic acids 1:8 and 1:5, it appears to be less important whether acetic acid or mineral acid be used.

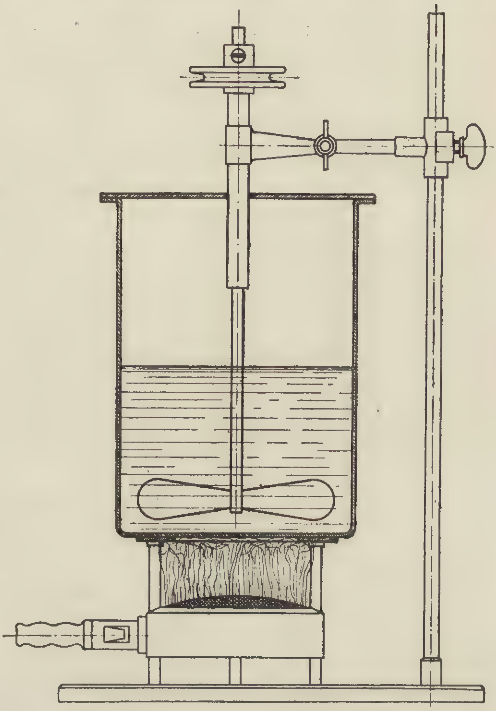


FIG. 5.—Apparatus with propeller-stirrer for reductions by Béchamp-Brimmeyr method.

As soon as everything is ready, the iron turnings are boiled up for five minutes, the nitro acid made faintly acid to Congo, and the latter solution is then allowed to drop in slowly through a dropping funnel, exactly as in the case of the sulphonation of naphthalene. It is absolutely essential that the mixture be kept boiling vigorously the whole time. A drop placed on filter paper should show no coloration, as this would indicate the presence of azoxy compounds which have a harmful action. The rate of reduction can be so arranged that the whole solution is run in during one hour. A considerable quantity of water, of course, evaporates off, so that the volume of the reduction liquid becomes diminished to two-thirds or less. When all has been added, the whole is boiled up with continuous stirring for another quarter of an hour, and is then allowed to cool somewhat. With good quality iron it may be noticed that hydrogen is evolved vigorously long after the reduction is complete, showing that cast-iron is attacked by water, even in the presence of iron salts. 10 Gms. of calcined soda are then sprinkled into the liquid with a teaspoon, until red litmus paper is turned strongly blue. (Caution : The solution readily froths over !)

10 gms. Na_2CO_3.

A test should also be made with sodium sulphide upon filter paper to ascertain whether all the iron has been precipitated. It is then filtered through a suction filter, the iron oxide remaining as a black velvety precipitate on the " nutsch," whilst the unused iron remains at the bottom of the pot ; the latter is then rinsed out into the filter and well washed. In the works the iron powder is allowed to remain in the reduction vessel, and is then used for the next operation. A good reduction liquor of the amino-naphthalene trisulphonic acid should be colourless or pale yellow, and in no case should it be reddish or brown. In the laboratory the solution is placed in a good porcelain dish, and is then evaporated down with direct heating to about $1\frac{1}{2}$ litres.

Formerly, it was the practice to melt up the product straight away to H-acid. This method, however, is rather barbaric, as by so doing not only is the required amino-acid melted up, but all the isomers as well. The yield was accordingly very unsatisfactory, about 80 % of theory of the total acids being obtained from one molecule naphthalene, which would use up 56 gms. of sodium nitrite. On melting the product it was not possible to obtain more than 55–60 % of theory of H-acid, and the product was very impure. It was therefore a distinct step forward when it became the practice to isolate the naphthylamine trisulphonic acid first, and then to melt the purified acid. At the present day all the works use this process, some of them recrystallizing the isolated acid from water.

In order to isolate the naphthylamine trisulphonic acid 1:8:3:6 the evaporated solution is placed in a glass vessel of 2 litres capacity. 200 gms. of common salt are added, and then, with continuous stirring, sufficient concentrated sulphuric acid to make the solution strongly acid to Congo paper. After a short interval, the solution practically solidifies owing to the separation of the acid sodium salt of the sulphonic acid. Stirring, however, must still be continued,

200 gms. Salt.

ca. 80 gms. conc. H_2SO_4.

and, as is so often the case, under the influence of the continuous movement the pasty mass finally becomes quite fluid again. After standing for at least 10 minutes, the precipitate is filtered off, and the vessel finally rinsed out with a portion of the filtrate. The precipitate must be well pressed down, and should be pure white. Its weight is about 700 gms., and corresponds to at least 70 gms. sodium nitrite. The mother-liquor would also use up about 30 gms. of nitrite, but is quite valueless. It is noteworthy that during the process of purification only the desired sulphonic acid is obtained together with quite a small quantity of isomers.

On melting the amino acid in question with alkali *H-acid* is produced (*aminonaphthol-disulphonic acid* 1:8:3:6), which is the most important dye intermediate of the kind, and is a good example of this type of operation.

To obtain H-acid in good yield the temperature must not exceed 190°, and the caustic soda used should be at least 30 %. The following charge will be found convenient for a laboratory melt :—

28 nitrite naphthylamine trisulphonic acid=about 280 gms. damp presscake.
130 gms. caustic soda.
130 gms. water.

28 Nitrite trisulph. acid.
130 gms. NaOH.
130 gms. Water. Total wt. about 540 gms.

This operation is carried out in an autoclave, a piece of apparatus which plays such an important part both in the laboratory and in the factory, that a special chapter is devoted to it (*q.v.*). It is charged with the given quantities of materials, and the melt is then carried out at 178–180° during 8 hours with continuous stirring, the pressure being about 7 atmospheres. After cooling, the autoclave is opened, any residual pressure being let off first by means of the valve. If the melt has been carried out correctly, the product will be of a somewhat dull dirty-yellow colour ; if it is too light, the melt was too short ; whilst if it is brown and smells very strongly of ammonia, the melt has been carried too far. At the same time, however, a certain amount of ammonia is always split off even with the most careful fusion.

The product obtained forms a syrupy mass which is mixed with granular crystals of anhydrous sodium sulphite, and after introducing into a stoneware jar of 2 litres capacity, it is diluted with 1 litre of water and acidified with 50 % sulphuric acid until it shows a strong and permanent mineral acid reaction with Congo paper ; care must be taken not to be deceived by the action of the free sulphurous acid which rapidly evaporates off (fume-cupboard !). The aminonaphthol disulphonic acid is precipitated in the form of fine white crystals, which are very sparingly soluble in a concentrated solution of Glauber salt.[1]

It is, however, preferable to allow the precipitate to stand for a few hours, to ensure that the separation is complete ; it is then filtered off, and the precipitate washed with 10 % brine to which 1 % hydrochloric acid has been added. Washing must not be carried on too long, otherwise some H-acid will be lost. Finally, it is pressed out well with a screw-press and dried at 100°.

The yield of 100 % *H-acid is about* 100 *gms., or approximately* 110 *gms. H-acid of* 86 % *purity.* (For quantitative estimation, see Analytical Section.)

Notes on Works Technique and Practice.—The sulphonation of naphthalene to the trisulphonic acid is nearly always carried out in steam-heated cast-iron boilers. As already noted, the mass heats up strongly on the addition of the monohydrate, and still more with the oleum, so that on the large scale the mixing of the substances takes considerably longer than in the laboratory. With a charge of 260 kgs. of naphthalene the preparation of the monosulphonic acid will take quite 1½ hours, even with the most careful cooling, and the addition of about 1000 kgs. of oleum will occupy more than 3 hours if one is to avoid the loss of large quantities of SO_3 by volatilization and the complete oxidation of considerable quantities of naphthalene.

By the use of a steam-jacketed vessel it is easy to regulate the temperature by allowing cold water to circulate through the jacket.

To save time, and to ensure that the vessels are always as full as possible, the nitration is carried out practically exclusively in one special vessel. The sulphonated mass is forced over by means of compressed air through a pipe into a nitrating pot that may have the form, for instance, given in Plate II. Cooling is carried out by means of water or ice, or, better still, by means of a cooling coil through which brine at −15° is circulating. In the latter case the vessel stands in concentrated salt solution. If ice is used it is a good plan to add some salt to the cooling liquid, and at the same time to get the freezing mixture well mixed by means of a stream of air introduced just beneath the surface, the cooling effect being thus

---

[1] Solubility of H-acid :—

at 18° in water	0·93 %.
at 18° in 10 % NaCl	0·053 %.
at 18° in 10 % NaCl+0·8 % HCl . .	0·023 %.

made more rapid. In the works, owing to the difficulty in cooling, the nitration is rarely carried out below 25°, and may occupy more than 8 hours. It must be noted here, however, that a thermometer may be registering only 25° whilst at the point where the nitric acid is run in the temperature may be considerably higher, although not shown by the thermometer.

In a well-conducted factory the nitrous fumes given off on dilution are, for the most part, condensed in water to give nitric acid ; for this purpose a fairly large plant is necessary, consisting of earthenware pots, filled with Guttmann balls or Raschig rings (*q.v.*).

The liming-out is always carried out in wooden vats, as shown in Plate VII. The gypsum is filtered off with suction or under pressure, and more recently it has been separated with considerable success by centrifuging. The centrifuges (Plate V.) are driven from beneath, and usually also can be emptied from the bottom. On the large scale they are made up to 1½ metres in diameter, and are so arranged that the "whizzed" gypsum, mixed with relatively little water, can be emptied direct into the tip-waggons.

The reduction of the large quantities of liquid also offers considerable difficulties. The reduction vessels consist of huge wrought-iron pots such as are shown on Plate IV. Owing to the scouring action of the iron, the bottom of the vessel must either be made easily removable, *e.g.* by screwing on a special base-plate that can be replaced easily when it gets used up, or, better, the bottom, and if necessary the whole vessel, is lined with acid-proof tiles. After the reduction is complete, a pipe is inserted and the contents blown over by compressed air into the filter-press. The turnings are pulverized in ball-mills.

The evaporation is always carried out in multiple-effect evaporators, triple-effect evaporators, similar to those employed in the beet-sugar industry, being used in the large German factories. The saving in coal as compared with evaporation under ordinary pressure is about 80 %. The precipitation and isolation of the naphthylamine trisulphonic acid require exactly the same apparatus as has been described for β-naphthalene monosulphonic acid (see Plates III. and VII.). As the press-cakes, pressed at 250 atmospheres, are stone-hard and very tough, they must be coarsely ground in breakers provided with toothed rollers, before being melted. At the same time the yield of titratable naphthylamine trisulphonic acid is determined in a definite portion. The melt is carried out in autoclaves provided with a manhole cover, thermometer-tube, and two manometers. Two reducing valves are always provided, so that in case one fails, there will always be one in reserve. (For further details see the general section on Autoclaves.) The so-called H-acid, even after it has been compressed by hydraulic means, still contains a large proportion of water (about 40 %). In the moist state it cannot be stored for long, as it rapidly oxidizes, and it is therefore either dissolved and the titrated solution then used at once in another portion of the works, or more usually it is dried in vacuo, and then ground up to the consistency of a fairly fine gravel. It is unwise to grind it too finely, as this increases the rate of oxidation, and the disintegrated H-acid dissolves with difficulty, a sticky paste forming on the sides of the vats. So far as I am aware the H-acid in nearly all factories is dried to allow of accurate calculation, as is the case with all similar products. Curiously enough, on the large scale the precipitation takes much longer than in the laboratory. For this reason the liquid must be allowed to stand for at least 12 hours after the addition of the acid, as otherwise considerable quantities of H-acid are lost. Many other cases are known of the slow precipitation of difficultly soluble precipitates, *e.g.* benzidine disulphonic acid, gallamide, gallic acid, etc. Presumably on the large scale considerably fewer nuclei for crystallization are present, so that for a given temperature the separation of large quantities takes a much longer time.

As a general rule, it may be noted that the melts of all sulphonic acids only go well when the salt content of the starting material is very slight; salt is practically a poison for alkali fusions, as owing to its insolubility in caustic soda it leads to scorching, and further it reduces the solubility of the resulting sulphite and of the sulphonic acid which is to be melted. It is quite possible to increase the yield of amino-naphthol sulphonic acids up to 90 % by careful attention to all the essential details. Frequently it is necessary to use potassium hydroxide in place of the cheaper caustic soda, and sometimes the fusion must be carried out in open vessels, as in the case of amino-naphthol sulphonic acid 1:8:4. In each case the most favourable conditions must be worked out first.

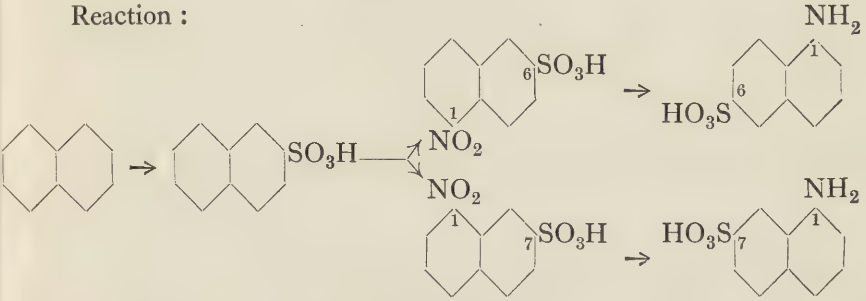
The caustic soda must be free from carbonate. It is dissolved in large batches and made up to 50 %. For use it is not weighed but is measured into the autoclaves by means of a measuring vessel. The liquor is stirred by means of compressed air and, owing to the danger of the stock solution freezing during the winter, the vessels containing it must be steam-heated.

The Glauber salt which is produced when H-acid or other acid is precipitated must be recovered as it has a considerable value. It is obtained by evaporating down the mother-liquors, and is frequently calcined; it may be used directly for diluting the dyes to the commercial strengths.

Naphthylamine Sulphonic Acids 1:6 and 1:7

(*Cleve's Acids*).

Reaction :



The naphthylamine sulphonic acids 1:6 and 1:7 have for long been of great technical importance. They serve for the manufacture of important black cotton colours of the type of Columbia Black FF, and also for the production of a whole series of substances of the developed colour type; for instance, the important Naphthogene Blue, Zambesi Black V, and similar products.

Sulphonic acids again of this type are also frequently made use of for colours such as Bayer's Benzo Fast Blue (*q.v.*).

In the present case the sulphonation is best carried out according to the method of O. N. Witt (in passing, it may be noted that this process has long been in practical use in the industry). Contrary to the β-naphthol sulphonation, an excess of sulphuric acid is used, but this does not, however, represent any financial loss, as a further addition of sulphuric acid is necessary later on, as we shall presently see. Exactly in the manner described on p. 6, 206 gms. of 92 % sulphuric acid (= 66° Bé.) are run into 128 gms. best quality naphthalene at 165°. The addition should occupy at least half an hour, as otherwise too much α-acid is produced, which is of no use for the process. The mass is then heated for a further half-hour at 165°, in order to convert as nearly as possible the whole of the α-acid into the disulphonic acid, thus obtaining at the end a mixture of 1:6 and 1:7 nitro acids which is practically free from isomeric α-acids. It is then cooled down to 60° and diluted with 150 gms. sulphuric acid of 85 %. (In actual practice at this stage the monosulphonic acid is blown over through a pipe into the nitrating vessel

206 gms. H_2SO_4, 66° Bé.
128 gms. Naphthalene.

by means of compressed air; in this vessel the sulphuric acid required for dilution has previously been placed. Care must be taken not to cool too much, as otherwise under certain conditions the β-sulphonic acid may solidify in the pipes, thus leading to awkward stoppages.) At approximately 55° the mass becomes so thick that it is almost impossible to stir it; the addition is now begun of 103 gms. of 60 % nitric acid (=1 mol.=40° Bé.). The mixture rapidly liquefies during the addition, each drop acting, so to speak, as a lubricant. After the addition of the first few grams there is no longer any danger of solidification, so that the temperature can be dropped to 25°, and, later on, even to 10° or 15° (55° is far too high).

103 gms. HNO_3 (60 %= 40° Bé.) = 1 mol.

In the laboratory a portion of the naphthalene sulphonic acid always separates out on to the sides of the vessel and the stirrer. For this reason it is absolutely necessary to scrape the vessel and the stirrer free from crust with a sharp iron spatula at least once during the operation, as soon as the consistency of the mass permits of this. If this precaution is neglected, it may easily happen that next day big lumps of β-naphthalene sulphonic acid will be found floating about in the liquid. On the large scale also attention must be paid to this point, and when necessary the solid portions detached. Since the mass behaves differently from the fluid sulphonation mixture of the 1:3:6-naphthalene trisulphonic acid, as we have seen, it is advisable not to use a glass stirrer, but one made of cast-iron or of iron rod about 10 mm. thick. Acid of the concentration used has, of course, practically no action on the iron. After all the nitric acid has been added, which will take about 2½ hours, the mixture is allowed to stand for at least a further 12 hours, and is then poured into 2 litres of water. Practically no nitrous fumes are evolved in this case.

The rest of the process may now be continued exactly as given for the reduction of nitro-naphthalene trisulphonic acid, *i.e.* liming, converting into the sodium salt by means of Glauber salt, reduction, and evaporation. This process, however, is not quite so easy in the present case, as the sodium salt of the Cleve acid 1:7 is very difficultly soluble, and consequently often separates out from the dilute reduction liquor. For this reason it is better in the present case to reduce the unchanged calcium salt, and then, after concentration, to precipitate the amino acids with hydrochloric acid.

Still neater, however, is a process which has long been in use by Bayer & Co. Instead of reducing the lime or sodium salt the magnesium salt is employed. For this purpose sufficient magnesite to combine with all the sulphonic acid is added before the addition

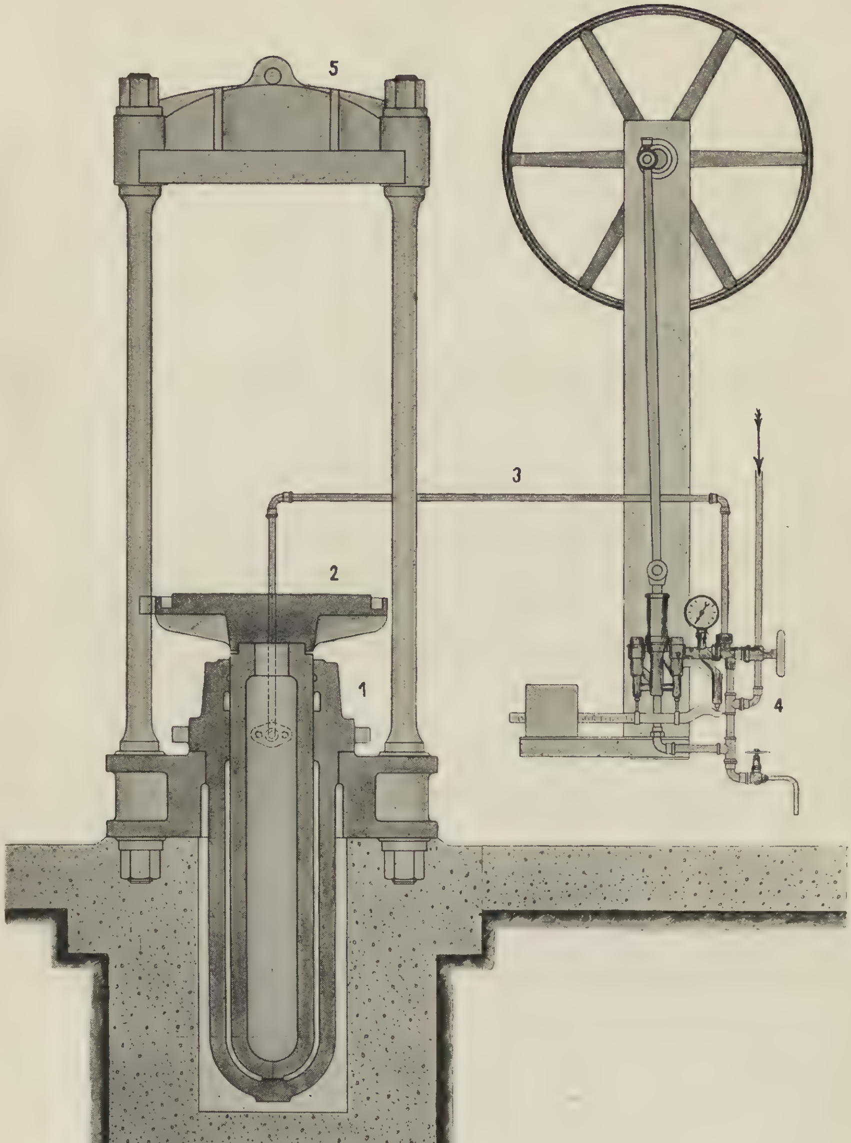


FIG. 8.—Hydraulic press and pump with automatic cut-out (made by Bucher-Mauz, Niederweningen, Canton Zürich). 1. Cast-steel cylinder. 2. Platform. 3. Pipe for compression water (250 atms.). 4. Pump with automatic cut-out at 250 atms. (The pressure may be varied by moving the weight; one pump can serve 4–6 presses easily.) 5. Cast-steel head-piece.

of the lime or chalk; in the present case 45 gms. $MgCO_3$ will suffice. The liming out is then performed exactly as given on p. 15. There are no further difficulties in the reduction, but great care must be taken that the best iron be used as the reduction of Cleve's acid readily stops at the hydroxylamine stage; either sulphuric acid or, better, acetic acid may be used for the reduction, which is carried out as described on p. 16. As soon as the reduction liquid has become quite colourless, sufficient magnesite or calcined magnesia is added to give a slight but distinct alkaline reaction to litmus. Since both magnesia and magnesite are very sparingly soluble a pronounced blue reaction cannot be given with the test paper. The product is then filtered, the iron oxide well washed, and the liquid evaporated down in a basin to 1 litre. The sodium salt of the 1:7-naphthylamine sulphonic acid is sparingly soluble, that of the 1:6, however, easily so.

45 gms. $MgCO_3$ about 320 gms. $CaCO_3$.

A strong solution of common salt is now added until the total concentration in the liquid is about 6 %. About 300 c.c. will be required. The sodium salt of the 1:7-acid is completely precipitated during the course of a day. The precipitate is filtered off and, after acidifying the mother-liquor with concentrated sulphuric or hydrochloric acid, the free 1:6-naphthylamine sulphonic acid is precipitated after standing several days. Both acids, the 1:7 as well as the 1:6, are somewhat impure because isomeric products are always formed in addition to the desired acids.

Modifications.—If it is desired to obtain quite pure Cleve acids, which will usually be the case, the process must be carried out somewhat differently. Instead of separating the 1:7 acid from the reduction liquor after evaporation by salting out with common salt, the whole may be made distinctly mineral-acid by means of sulphuric or hydrochloric acid; in the course of two or three days a thick precipitate of a mixture of the 1:6- and 1:7-naphthylamine sulphonic acids will be formed, which is thoroughly washed on a suction filter with cold water. The mother-liquor is coloured violet and always contains hydroxylamines. It will use up to 20 gms. sodium nitrite on diazotization, corresponding to about 28 % of theory of the sulphonic acid. With careful working, however, and especially by paying special attention to the reduction, the losses may be diminished to less than 20 %. After protracted washing on the filter the acids become quite pale in colour. A small portion of the sulphonic acids is lost by so doing, but a particularly pure substance is obtained in this manner.

The Cleve acids, washed free from impurities, isomers, and

1 l. water.
ca. gms. Na_2CO_3.
50 gms. NaCl.

disulphonic acids, are now dissolved in 1 litre of water and about 35 gms. soda. 50 Gms. of finely powdered common salt are then added quickly to the hot soda solution of the mixture, which is then allowed to stand for one day with continuous mechanical stirring. The Cleve acid 1:7 separates out in an extremely pure form as the sodium salt, which is filtered off and washed with a very little ice-cold water, after which it is pressed.

The mother-liquor from the 1:7 acid is acidified as described above, and gives a good 1:6 acid. For complicated azo-colours, such as Columbia Black FF, Zambesi Black V, and so forth, it is, however, advisable to purify this product once more by solution and reprecipitation. The purer the intermediate, the greater the yield of finished colour.

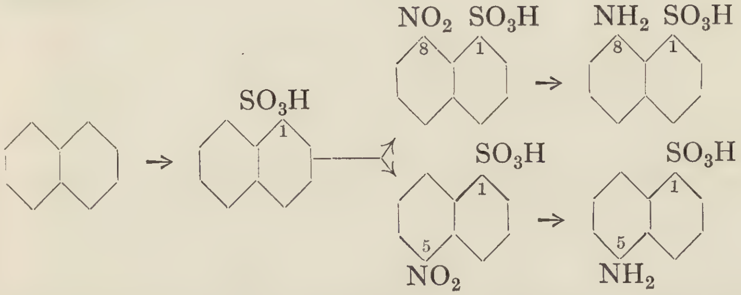
Yield:	Cleve acid 1:7 . .	70 gms.	(M.W. 223).
	,, ,, 1:6 . .	80 gms.	,,

Notes on Works Technique and Practice.—The same considerations hold good for the sulphonation of naphthalene in quantities of 200–300 kgs. and over as were noted in discussing H-acid. Here, also, the sulphonation takes much longer than in the laboratory, corresponding to the larger quantities used. Again, the reduction must be watched very carefully, as the Cleve nitro-sulphonic acids are much harder to reduce than the naphthalene nitro-polysulphonic acids. The partially reduced acids are hydroxylamine sulphonic acids, which appear finally in the mother-liquors and render the Cleve 1:6 acid in particular very impure; but if the reduction is carried out very exactly the crude 1:6 acid will be fairly pure. On the large scale the mother-liquors are always evaporated down separately, and a second crop of crystals obtained which require about 10 parts of nitrite per molecule, corresponding to about 30 kgs. impure sulphonic acids.

The red coloration which nearly always appears on leaving impure Cleve acids exposed to the air in the presence of moisture, is caused exclusively by the oxidation of the hydroxylamine acids. Pure Cleve acids are stable in air and give almost identical azo dyes. The observation is often made that the 1:7 acid affords better yields of colouring matters. This is quite correct, but does not depend, however, on the 1:7 acid as such, but upon the fact that this acid is separated as its sodium salt, and is therefore much purer than the 1:6 isomer which is obtained as the free acid. According to my own experience, a pure 1:6 acid yields dyes identical in strength and shade with those from the 1:7 acid. The differences in shade which are frequently observed are so insignificant that they come within the limits of technical errors.

Naphthylamine Sulphonic Acids 1:5 and 1:8.

Reaction :



The preparation of the naphthylamine sulphonic acids 1:5 and 1:8 is closely connected with that of the Cleve acids. They are amongst some of the most widely used intermediates.

In order to obtain the α-sulphonic acid, it is preferable to carry out the sulphonation at a temperature below the melting-point of naphthalene (below 80°). 128 Gms. of very finely divided naphthalene [1] are rapidly added to 260 gms. of sulphuric acid (monohydrate) at 0°. The sulphonation begins at once, and if the mixture be left to itself after the addition it will solidify suddenly to a cement-like mass as soon as the first crystals of the naphthalene sulphonic acid begin to separate. The laboratory stirrer is incapable of dealing with this hard mixture and will stop ; it is therefore a good plan to inoculate with a small quantity of solid α-acid as soon as the naphthalene has been added. The material for this inoculation may be prepared by warming a small portion of naphthalene with sulphuric acid on the water-bath and then cooling the mixture. This inoculation causes the sulphonic acid formed to separate out at once, and prevents it from crystallizing out from the super-saturated solution. The sulphonation mixture, therefore, thickens slowly, and a sudden solidification is no longer to be feared.

128 gms. Naphthalene.
260 gms. H_2SO_4 (100 %).

The temperature rarely rises above 35°, for which reason it is necessary to use pure monohydrate, or else part of the naphthalene will remain unattacked. In any case, however, it will be found that a small portion escapes sulphonation on occasions. When this occurs the mass should be heated to 60° on the water-bath and stirred until all the naphthalene has disappeared. It is, however, by no means easy to carry out the sulphonation smoothly on a small scale, and a fair amount of practice is required for such operations. In order to ascertain how much naphthalene there is in the sulphonation mixture a small portion should be dissolved in water, when the unattacked naphthalene separates out on the bottom of the test-tube. On the large scale no difficulty is found in carrying out this sulphonation.

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[1] 96 % of the ground substance should pass through a sieve having 400 meshes to the square cm.

103 gms. HNO_3. 60%= 40° Bé.
45 gms. $MgCO_3$
about 320 gms. $CaCO_3$.
300 gms. Fe.
20 c.cs. Acetic acid (40 %).
½ l. Water.

The nitration is carried out exactly as for the preparation of Cleve acid, except that it is, in this case, unnecessary to add a second quantity of sulphuric acid as the whole amount is added at the start. The reduction and separation of the two isomeric naphthylamine sulphonic acids is also effected as described for Cleve acid. The sodium salt of the 1:8 acid is even more insoluble than that of the 1:7 acid, so that the separation is still easier in this case. A 1:8 acid is obtained which is practically free from Cleve acids, with the exception of very small quantities which are always formed in spite of the low temperature of sulphonation.

The yield of 1:8 *acid is about* 100 *gms. of* 100 % *product* (*M.W.* 223); *whilst that of the* 1:5 *acid, which is obtained by precipitating with sulphuric acid, amounts to* 40 *gms. of* 100 % *product* (*M.W.* 223).

260 gms. Fe.
40 gms. Fe.
About 60 gms. conc. H_2SO_4.
40 gms. Magnesite.

Modifications of the Process.—The naphthylamine sulphonic acids 1:5 and 1:8 are distinguished from other acids by the fact that they can also be isolated in the presence of considerable quantities of iron salts. Instead of liming out and then reducing the magnesium salt, the nitro acids may be diluted with water, and then allowed to run on to iron turnings, with vigorous stirring. Care must be taken, however, that the solution remains neutral to Congo; it heats up to 80°, but no sulphonic acid separates out. Only after heating the finished reduction mass for some time to boiling does the violet coloration gradually give place to a greenish one. 40 Gms. of iron powder are added cautiously, whilst the liquid is heated at the boiling-point until the ferrous salts of the 1:5 and 1:8 acids separate out as greyish-white crystals. After cooling these are decomposed by means of sulphuric acid until the liquid is distinctly mineral acid. The free sulphonic acids are filtered off, the ferrous sulphate is well washed out, and the residue dissolved with the aid of 40 gms. of magnesite. The filtered magnesium salts on salting out with 10 % of common salt (calculated on the amount of liquid) yield an extraordinarily pure 1:8 acid, which is completely free from Cleve acid. The filtrate from the sodium salt of the 1:8 acid gives, on acidifying, an extremely pure 1:5 acid, as the Cleve acids are only reduced to the hydroxylamine stage, and are washed away with the iron sulphate.

Notes on Works Technique and Practice.—On the works scale the sulphonation of the finely powdered naphthalene must be carried out in a manner somewhat different from the laboratory methods. First of all, it is necessary to make use of freshly-ground naphthalene, as it rapidly cakes together. The best way is to run the mass through the disintegrator on the previous evening, and then to run it through once more, or twice more if necessary, immediately before the sulphonation; it must then be added to the sulphuric acid as rapidly as possible. For this purpose it is very convenient to heap up the naphthalene in an open box from which it may be transferred to the vessel by a wooden shovel. To ensure that no lumps of the snow-like substance get into the acid a coarse sieve provided with a funnel should be placed over the opening into the vessel. As soon as all the naphthalene has been added the mass is " seeded " and the sulphuric acid and naphthalene mixed at once by means of an iron stirrer of the anchor type, as shown in Plate II. In spite of careful cooling the temperature of the porridge-like mass rises slowly to 18°, and then suddenly, owing to the heat of crystallization, it rises to about 58°. For this reason the action of the sulphuric acid is considerably more energetic in this case than in the laboratory, so that it is necessary to dilute the monohydrate with 3 kgs. ice to about 98 %. The naphthalene disappears completely in the course of 1½ hours if it has been finely enough powdered. The reduction is carried out as given under H-acid, as also is the evaporation of the reduction liquor.

If the modified process be used iron reduction vessels cannot, of course, be utilized, and it is found to be most convenient to adopt wooden tubs, which last a long time.

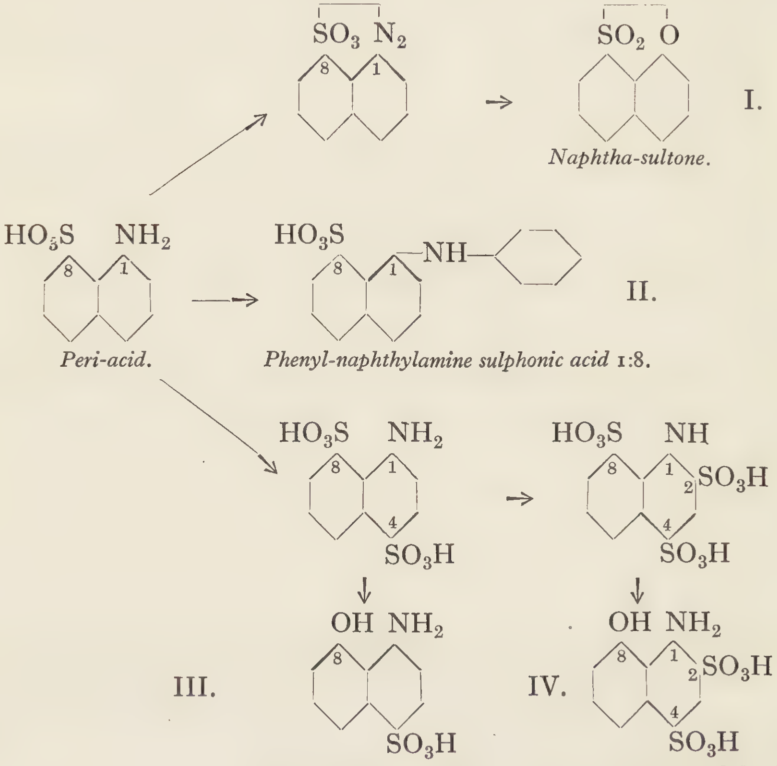
The filtration of the free sulphonic acids, which have been precipitated by means of sulphuric acid, is effected by means of filter-presses using felt filters. The better the product has been washed out, the easier is the extraction by means of magnesia. It is advisable, however, to boil out the residue with water once or twice more, as otherwise considerable quantities of the acid may be lost in the magnesia-iron sludge.

On the large scale it is not usual to precipitate the 1:8 acid as the sodium salt by simply sprinkling in common salt, but instead a solution of salt is allowed to run in during an hour (otherwise some

1:5 acid will be carried down with it). Both methods appear, however, to be of about the same value.

The 1:8-naphthylamine sulphonic acid or peri-acid is not used directly as such for the preparation of dyes, but is first converted into various other compounds. The most important of these are *Naphtha-sultone*, *Phenyl-naphthylamine sulphonic acid* 1:8 (Phenyl-peri-acid), and the *Amino-naphthol sulphonic acids* 1:8:4 and 1:8:2:4.

Their method of formation is shown in the following scheme :—



I. *Naphtha-sultone.*

Peri-acid.

II. *Phenyl-naphthylamine sulphonic acid* 1:8.

III. *S-acid, or amino-naphthol sulphonic acid* 1:8:4.

IV. *Amino-naphtholdisulphonic acid* 1:8:2:4. *Chicago-acid, or SS-acid.*

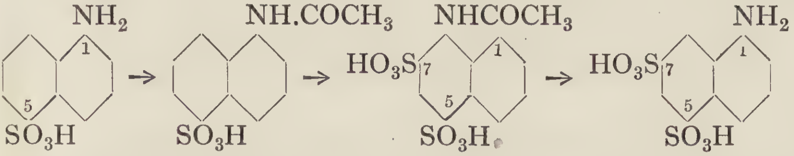
The naphthylamine sulphonic acid 1:8 may be converted into the diazo compound on treatment with nitrous acid (sodium nitrite) in mineral acid solution at 25°. On heating this in aqueous solution to 55° a quantitative yield is obtained of naphtha-sultone (I.). The yield of sultone obtained is a direct measure of the purity of the starting material ; it is practically always converted into the naphtha-sultone sulphonic acid which, on coupling with azo components, yields dyes which are very pure and fast to light. During recent years, however, the importance of these colouring matters has diminished considerably.

Again, the naphthylamine sulphonic acid 1:8 may be converted into its arylated derivatives ; thus the technically important phenyl-naphthylamine sulphonic acid 1:8 may be obtained by heating the free naphthylamine sulphonic acid with aniline (II.).

One part of the free sulphonic acid is heated with three times its weight of aniline (or *p*-toluidine) to 160° in an enamelled vessel, which is heated in an oil bath. The water, which is always present in the substance, is distilled off in vacuum, the product being afterwards heated for 24 hours with continuous stirring. The excess of aniline is carefully distilled off, the aniline salt of the resultant phenylated acid is then decomposed by means of the calculated quantity of soda-lye, and the residual aniline is driven off with steam, thus obtaining a solution of the phenyl-naphthylamine sulphonic acid, which is then coupled directly with diazotized H-acid in acetic acid solution. If the process has been correctly carried out, the acid itself need not be isolated. The resultant dye is *Sulphon Acid Blue R* (Bayer), which is fast to light.

If the naphthylamine sulphonic acid is sulphonated with oleum, the di- or tri-sulphonic acid is produced (or the anhydro compounds, the *Naphthasultams*) according to the strength. These two products are fused with caustic potash in an open pan at 200–210°, and yield the corresponding amino-naphthol sulphonic acids (III. and IV.). Both are intermediates for the production of wool and cotton colours.

Naphthylamine sulphonic acid 1:5 is of less importance, and can only be dealt with briefly. It is either diazotized and coupled with amines and naphthols, or is worked up into amino-naphthol sulphonic acid 1:5:7.



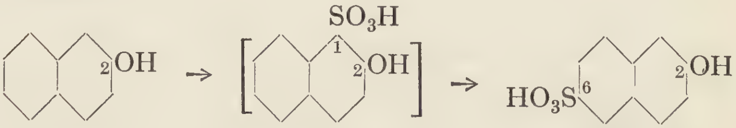
As indicated in the above scheme, the 1:5 acid differs from the 1:8 acid, in that it must be acetylated before sulphonation, as it is otherwise destroyed by the sulphuric anhydride. Acetylations of this kind play a not unimportant part in the technology of dyes (cf. *Amidonaphthol Red G*).

Sulphonation of β-Naphthol

On sulphonating β-naphthol a considerable number of mono- and poly-sulphonic acids are obtained according to the concentration and the temperature of the sulphuric acid used. Only a few typical cases will be discussed, in order that the beginner may be able to arrive at an idea of this branch of manufacture of intermediate products.

As is well known, β-naphthol sulphonates chiefly in the 6-position on treatment with sulphuric acid of 66° Bé. (93 %); that is to say, naphthol sulphonic acid 2:1 is first formed, which is rapidly isomerized to the 2:6 acid (Schäffer acid).

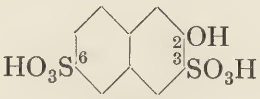
Reaction:



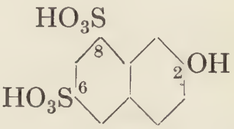
Schäffer acid.

If an excess of acid be used, a certain amount of the 2:3:6 and 2:6:8 acids are always formed as well which, owing to their property of combining with diazonium compounds to give respectively reddish or yellowish dyes, are usually known by the names of R-acid and G-acid.[1]

Formulæ:



R-acid.



G-acid.

According to whether the sulphonation is warm or cold, relatively more R- or G-acid is formed respectively. All three of the acids in question are important intermediates for the production of azo colours. As it is absolutely impossible to obtain the three isomers by themselves, it becomes necessary to separate them very carefully from their mixture.

It is important to emphasize the fact that the β-naphthol which is to be used must be powdered. If this elementary precaution be neglected, that portion of the naphthol which first enters into reaction becomes sulphonated at the expense of the coarse lumps, which swim about in the reaction mass, and it is impossible to obtain uniform results. This will also be the case if the reaction mixture be allowed to stand instead of being continuously stirred. The apparatus is the same as that for β-naphthalene sulphonic acid.

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[1] German: Rot = red; Gelb = yellow.

Naphthol Sulphonic Acid 2:6 *and Disulphonic Acid* 2:3:6 (*Schäffer Acid and R-acid*).

200 gms. H_2SO_4, 100 %.
142 gms. β-naphthol.

142 Gms. (1 mol.) of pure, finely powdered β-naphthol are added to 200 gms. of 100 % sulphuric acid with stirring. The temperature rises rapidly to about 80°, at which it is left for about a quarter of an hour to ensure a homogeneous mixture. The temperature is then raised to 100–110°, stirring continuously, until a test portion no longer shows any separation of β-naphthol on pouring into water. This will occupy about 3 hours. The mixture is then poured into 1 litre of water, and is neutralized with about 200 gms. calcium carbonate. A warm solution of Glauber salt is now added to the pasty gypsum mixture. A clear, filtered test portion should not give any turbidity with Glauber salt. The whole is then filtered and the gypsum washed out. (For this purpose the factories make use of waste Glauber salt from the H-acid or other caustic soda melt, which they can obtain at less than 1 franc per 100 kgs.) The sodium salts are evaporated down in a porcelain dish over a bare flame to half a litre (a vacuum is used in the works) and the relatively sparingly soluble sodium-2:6-sulphonate salted out with sufficient common salt for the solution to contain 20 % of salt (in the present case 100 gms.). With good stirring the Schäffer salt separates out completely during the course of a day. It is filtered off and washed with a very little concentrated brine. The aqueous solution of the Schäffer salt purified in this manner should show only slight fluorescence. The filter cakes are well pressed in a screw-press and consist of very pure Schäffer salt, containing only a very little R-salt. The mother-liquor is acidified with concentrated sulphuric acid and allowed to stand for some time. In the laboratory, 10–12 hours will suffice, but on the large scale several days are required, before the acid sodium salt of R-acid has separated out completely. It is extremely easily soluble, so that in some circumstances the mother-liquor itself can be coupled directly with an azo component to a dye of the Ponceau series (*e.g.* with meta-xylidine to give Ponceau R).

200 gms. $CaCO_3$.

100 gms. Salt.

If it is desired to obtain more R-acid than Schäffer acid the quantity of sulphuric acid is increased, so that finally 2:3:6-naphthol-disulphonic acid is obtained almost exclusively.

Yield :

160 gms. Schäffer salt (100 %) approximately.
80 gms. R-salt (100 %) approximately.

The method for the determination of R-salt and Schäffer-salt is given in detail in the analytical portion.

2:3:6- *and* 2:6:8-*Naphthol-disulphonic Acid* (*R-salt and G-salt*).

G-salt has long been a much more important product than R-salt owing to the fact that the former acid is the starting-point for amino-naphthol-sulphonic acid 2:8:6 (Gamma-acid), which is used in increasing quantities for the production of a large number of wool and cotton dyes. The preparation of this substance is by no means simple, for which reason the various German works which manufacture γ-acid have signed a convention which binds them not to sell it to outsiders below a certain price, which before the war was about four francs per kilo.

The naphthol-sulphonic acid 2:6:8 can be readily converted into the corresponding amino-naphthalene sulphonic acid, thus obtaining amido-G-acid, which affords a good yield of γ-acid when fused with caustic soda. Instead of starting from the naphthol-disulphonic acid, the naphthylamine sulphonic acid may equally well be used, which is obtained by the direct sulphonation of β-naphthylamine. The diagram on p. 36 illustrates these various relationships more clearly than any description. On the same page full details as to the preparation of the isomeric β-naphthylamine sulphonic acids are given, and of their fusion with alkalis.

142 gms. β-naphthol. 420 gms. H_2SO_4, 100 %.

Since more G-acid than R-acid is obtained at lower temperatures, it is necessary, in order to obtain the former acid, that a temperature of 30–35° should not be exceeded, which necessitates the use of a somewhat larger excess of sulphuric acid. Again it is necessary to powder the naphthol finely ; it is then added slowly to three times its weight of sulphuric acid (monohydrate), the temperature being kept as low as possible by careful cooling. It must be remembered, however, that whilst the thermometer may show for example 20°, overheating may nevertheless occur where the β-naphthol drops into the acid. This is particularly the case on the large scale, where, for instance, at least 5 hours must be allowed for the addition of 288 kgs. naphthol. Cooling by means of circulating brine is by far the best method.

The sulphonation, in distinction from that for R-acid, does not occupy merely a few hours, but frequently takes 2–4 days. Stirring must be continued until a test portion diluted with a very little water no longer gives any precipitate. If this is not the case within two days it is best to add a little more monohydrate or, very cautiously, a very little fuming sulphuric acid containing not more than 15 % SO_3. The sulphonation is then finished after a further 2–3 hours.

The sulphonated product is poured into a litre of water and treated with lime or chalk as given under R-acid. The calcium salt is not decomposed by means of a sodium salt, but either potassium carbonate is added to its solution until all the lime has been precipitated as chalk, or more cheaply commercial 90 % potassium sulphate is employed. The filtered solution of the potassium salt so obtained is, in the laboratory, evaporated down over a bare flame to 400 c.c. (for 1 gram-mol.). Sufficient hydrochloric acid is added to render the product strongly mineral acid, about 100 grams being required. On cooling, the acid potassium salt of the naphthol-sulphonic acid 2:6:8 separates out in a completely pure form, and after standing for a day (or 1–2 days on the large scale), it is filtered off, washed with a little 10 % potassium chloride solution, and well pressed. Centrifuging is the best means for extracting as much mother-liquor as possible. The mother-liquor containing all the R-salt is either salted out with 150 gms. common salt, or may be worked up directly into colour.

1 l. water.
420 gms. $CaCO_3$.

ca. 150 gms K_2CO_3 (comm.).

About 100 gms. HCl.

Yield from 142 gms. β-naphthol :
about 160 gms. G-salt (acid potass. salt, M.W. 341)
about 145 gms. R-salt (M.W. 341).

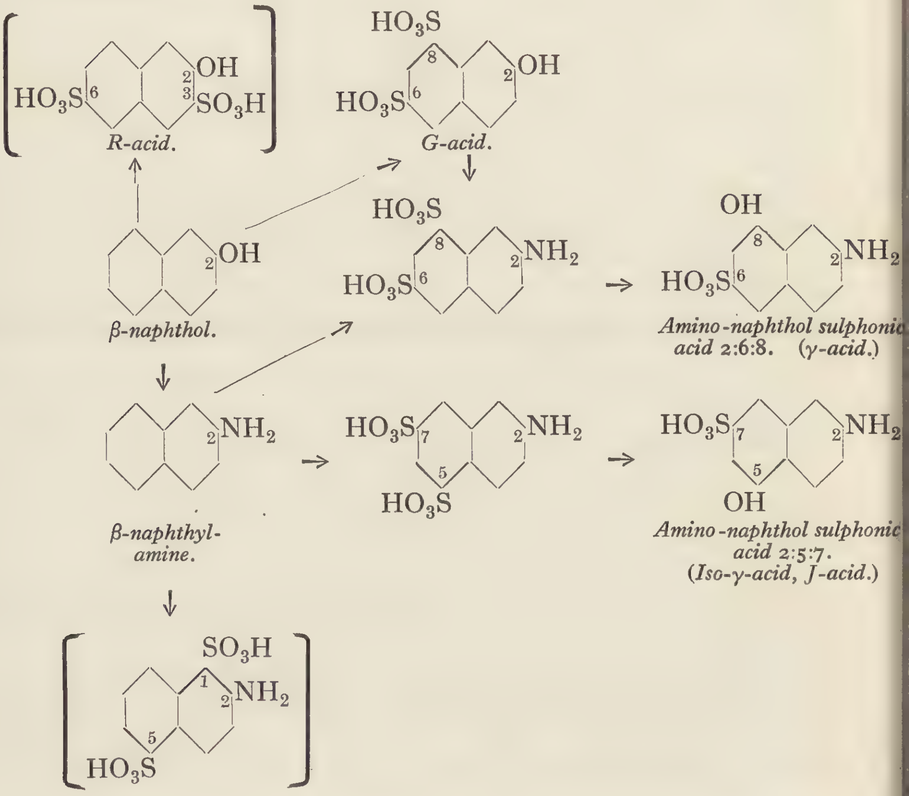
Amino-naphthol Sulphonic Acids 2:6:8 and 2:5:7 (γ-acid and J-acid), from β-naphthylamine.

γ-acid is always prepared from β-naphthol by one of two methods. Either the so-called G-salt (*cf.* p. 32) is converted into amido-G-salt by heating with 20 % ammonia to 240°,[1] the latter being then melted to γ-acid ; or the β-naphthol is first converted into β-naphthylamine (*q.v.*), which on disulphonation gives amido-G-acid and other isomers. The method for the separation of these acids is described in detail in the next few pages, as also the melt of the pure amino-disulphonic acids. The diagram on the next page will explain the above statements.

[1] Caution. Pressure about 50 atmos.

β-Naphthylamine Disulphonic Acids.—On sulphonating β-naphthylamine at least three isomers are always produced, as may be seen from the following scheme. The separation is by no means easy, and can only be carried out in the laboratory by maintaining certain very exact conditions. On the works scale it is easier to carry out as, owing to the larger quantities dealt with, the fractional crystallization can be more readily supervized.

Reactions :


R-acid.
G-acid.
β-naphthol.
β-naphthylamine.
Amino-naphthol sulphonic acid 2:6:8. (γ-acid.)
Amino-naphthol sulphonic acid 2:5:7. (Iso-γ-acid, J-acid.)
HO₃S
OH
SO₃H
NH₂

We start with the completely dry β-naphthylamine sulphate as obtained by precipitation from the hydrochloride in the preparation of β-naphthylamine (*q.v.*). The quantitative estimation of the sparingly soluble sulphate is carried out by dissolving a weighed portion in concentrated sulphuric acid at 60°, pouring the clear solution into water, and adding 1 c.c. of hydrochloric acid. Without the addition of hydrochloric acid it is practically impossible to diazotize the substance. β-naphthylamine sulphate which has been properly made should be about 97 % pure.

192 Gms. of the sulphate (=1 gm.-mol.) is ground up very fine, well rubbed up with 1 gm. of calcined soda, and then added to 560 gms. of sulphuric acid monohydrate at a temperature of 30–60°. It is then heated at 65° until a test portion gives a clear solution with soda; this should take about an hour, the whole time occupied from the first addition to complete sulphonation being about 3 hours.

192 Naphthylamine sulphate.
560 gms. H_2SO_4, 100 %.

A process suggested for obtaining the 2:5 acid in a pure condition as the sodium salt consists in liming, treating with soda, evaporation, and extraction of the dry salts with 95 % alcohol.[1] This method is actually carried out, and is strongly to be recommended if it is simply a question of obtaining the 2:5 acid in a pure condition. If, however, the disulphonic acids are to be prepared this expensive separation is unnecessary, and the crude product is simply sulphonated straight away.

The mixture of the isomeric monosulphonic acids is cooled down to 40° with continuous stirring, and is then treated cautiously with 500 gms. of oleum (66 % SO_3) during 2 hours, the temperature not being allowed to exceed 55°. The sulphonation is continued until a test portion dissolves readily and completely in a little ice-water without any subsequent turbidity; this is absolutely necessary if the later separation of the mixture is to be successful. When the sulphonation has gone thus far, it must not be stopped, but must then be allowed to continue at 55–65° for several hours, as it has been found that only in this way can success be assured; only when the mixture has been thoroughly sulphonated does the separation succeed. Too strong an oleum must not be used, as otherwise too much substance is destroyed, and the temperature of the sulphonation must not exceed 65°. This operation will last about 2 days, and must not be hurried. The sulphonated mixture, which still contains a little free SO_3, is poured in a thin stream into a mixture of 950 c.cs. of water and the same quantity of ice, with good stirring, during 5 minutes. The mixture becomes very hot, and the temperature is accurately followed with the thermometer, the rate of addition being such that the end volume will be exactly 2600 c.c. and the temperature 60°; this is easily done with a little practice.

500 gms. Oleum; 60 % SO_3.

950 c.cs Water.
ca. 1 kg. ice

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[1] The sodium salt of the 2:5 acid is easily soluble in 95 % alcohol, whilst those of the 2:7 and 2:8 acids are soluble with difficulty; *cf.* D. R. P. 39925 and 29084.

The reason why these and similar figures must be so carefully observed lies in the following: If the temperature rises too high, the naphthylamine disulphonic acid 2:1:5 decomposes and splits off a sulphonic group; the 2:5 acid then precipitates out and carries other acids down with it. If the temperature is too low, the naphthylamine disulphonic acid 2:5:7 separates out, which is also undesirable.

The mixture is now allowed to cool down to 40° with continuous stirring. The vessel, which must not crack, is placed in warm water. Within 5 hours the hydrate of the naphthylamine disulphonic acid will have separated out in a completely pure form, whilst all the remaining sulphonic acids stay in solution. It is then filtered off quickly through as large a "nutsch" as possible, fitted with a good double filter paper, so as to prevent the solution from cooling too rapidly. The press-cakes, which have a sulphuric acid content of about 35 %, are well pressed with a screw-press and the filtrate united with the other filtrates: *Press-cake I.* (about 200 gms.).

During the course of the next day a completely pure naphthylamine disulphonic acid 2:5:7 separates out at 15°, which again is filtered off and pressed: *Press-cake II.* (about 70 gms.).

The filtrate from this second crystallization is exactly neutralized with chalk, as described under H-acid (pp. 15-16), converted into the sodium salt by the addition of the necessary quantity of soda, and the filtered liquid evaporated down to 750 c.cs. After standing several days the sparingly soluble sodium salt of naphthylamine disulphonic acid 2:1:5 separates out and is filtered off and dried: *Press-cake III.* (about 70 gms. dry substance).

ca. 25 c.cs.
30 % HCl.

The solution freed from the 2:1:5 salt is now evaporated down further to $\frac{1}{2}$ a litre, and is then acidified with 25 c.cs. of hydrochloric acid. Again a practically pure naphthylamine disulphonic acid 2:5:7 separates out: *Press-cake IV.* (about 45 gms.).

700 c.c.
Water.
70 gms.
NaCl.

Press-cake I. (about 200 gms. dry substance) is dissolved in 700 c.c. of water at 100° and treated with 70 gms. of salt. The monosodium salt of the pure naphthylamine disulphonic acid 2:6:8 separates out to such an extent that the contents of the vessel become solid. The cakes are crushed, filtered after 12 hours, and well pressed. *The dry substance weighs about* 145 *gms. and titrates about* 29 *gms. nitrite.* Similarly with press-cakes II. and IV., which are dissolved in about five times their weight of boiling water and precipitated with half their weight of common salt. *Total yield about* 100 *gms.* (= 21 *gms. nitrite*).

PLATE IV.

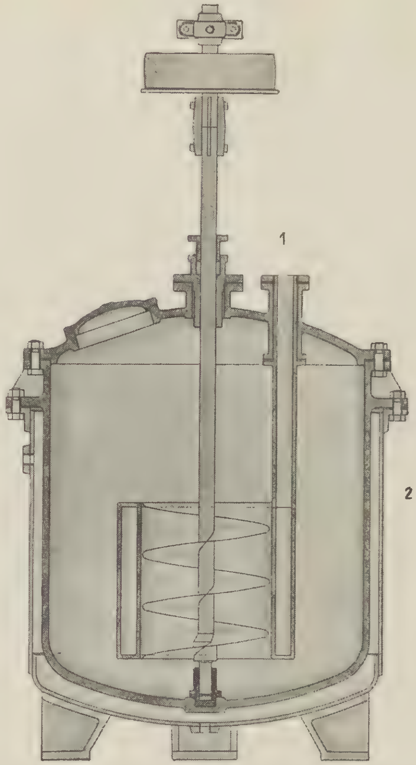


FIG. 10.—Nitrating pot with helical stirrer, provided with internal and external cooling. 1. Inlet tube for internal cooling water. 2. Jacket for heating or cooling.

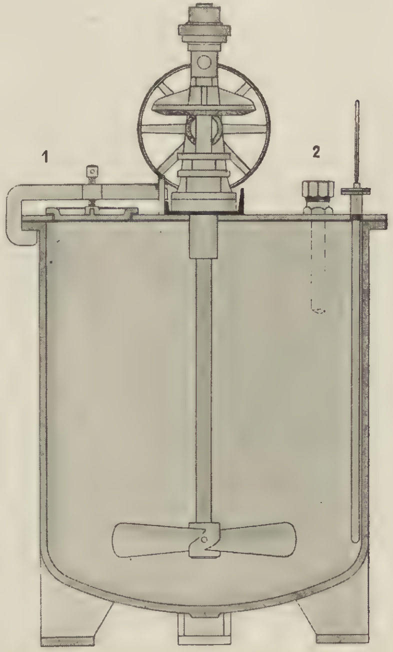


FIG. 11.—Reduction pot with propeller stirrer (scale 1 : 30). 1. Manhole for charging. 2. Connection for exit-tube.

The 2:1:5 *acid titrates at about* 3·5 *gms. nitrite*, and is very impure owing to the presence of other salts. The various mother-liquors are kept separately, they titrate about 11 gms. nitrite, but cannot be fractionated in the laboratory.

The pure sulphonic acids are distinguished by a very characteristic fluorescence, which can, however, only be seen clearly with very pure products, as otherwise they are hidden by the fluorescence of the 2:6:8 acid. The 2:6:8-*naphthylamine disulphonic acid* fluoresces *blue*, the 2:5:7 *acid green*, and the 2:1:5 *acid red.* Further, the 2:6:8 and 2:5:7 acids show a different behaviour with an acetic acid solution of diazotized nitraniline; the 2:6:8 acid gives only a faint yellowish coloration in dilute solution due to the formation of a diazoamino compound, whilst the 2:5:7 acid, on the contrary, yields at once a true red azo colour. It is therefore possible to gain an idea as to the purity of the products from the intensity of the colorations. Again, the diazotized 2:6:8 acid forms a very difficultly soluble red azo dye with R-salt which is precipitated at once even at great dilution and dissolves with a red colour on boiling, whilst the 2:5:7 acid gives an orange-red dye which is easily soluble.

Notes on Works Technique and Practice.—The addition of soda to the substance which is to be sulphonated is made solely for the purpose of preventing the formation of lumps on mixing with sulphuric acid; the mixture is broken up by the carbonic acid given off and very small quantities of soda suffice. In the factory the process is often carried out somewhat differently from that given above. Instead of sulphonating with monohydrate, the sulphate or the free β-naphthylamine base is added directly to 40 % oleum. Also less monohydrate is used as a diluent; the reasons for this are the same as those already given (*cf.* p. 11). In a well-conducted works the isolation of the various sulphonic acids is comparatively easy, as the individual acids can be better separated when working with large quantities than in the laboratory. Filtration is usually carried out by means of wooden filter-presses fitted with so-called nitro-filters (*q.v.*). The purified acids, or their acid salts, may be centrifuged with advantage. The various mother-liquors, which on the laboratory scale contain an inseparable mixture of acids, are worked up either separately or mixed together according to the degree of purity. For this purpose they are neutralized completely with soda and "*evaporated down to salt,*" that is to say, they are evaporated down in a multiple-effect vacuum concentrator until the sparingly soluble sodium chloride is precipitated out; the latter is then always centrifuged and the mother-liquors returned to the process. It is found that during the sulphonation a certain amount of diazotizable nitrogen always disappears ; this is to be attributed partly to the direct combustion of the substance, and partly to the formation of very easily soluble sulphones or sulphamides, the presence of which is readily noted owing to their yellow colour.

The 2:5:7 and 2:6:8 acids are melted with caustic soda to the corresponding aminonaphthol sulphonic acids, or, more rarely, they are sulphonated further. The 2:1:5 acid, however, is either worked up directly to light-resistant azo colours of the Lithol Red type, or it is sulphonated a stage further and is then fused to give aminonaphthol disulphonic acid 2:5:1:7.

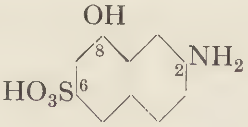
The total yield of titratable naphthylamine disulphonic acids is very satisfactory. Approximately the following quantities are obtained from 1 molecule of β-naphthylamine or from the corresponding quantity of β-naphthylamine sulphate :

1 *Molecule* (= 69 *gms. sodium nitrite*) *yields about*

29	*nitrite as*	2:6:8-*naphthylamine disulphonic acid*	
20	,,	2:5:7 ,, ,,	two separate fractions.
3·5	,,	2:1:5 ,, ,,	
11	,,	*as residual acids=mixture of various isomers.*	

Total=63·5 *nitrite as definite disulphonic acids*=92 % *of theory. Products equivalent to about* 3·5 *nitrite remain unaccounted for.*

Aminonaphthol Sulphonic Acid 2:8:6 (γ-Acid). M.W. 239.



35 gms. Nitrite. 2:8:6-Naphthylamine disulphonic acid. *ca.* 180 gms. 220 gms. NaOH. 120 gms. H_2O.

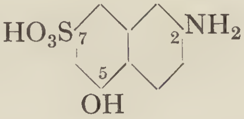
The melt of the pure naphthylamine disulphonic acid offers no special difficulties so long as the acid is as free as possible from sodium chloride (*cf.* p. 22).

A quantity of naphthylamine disulphonic acid 2:6:8 equivalent to 35 gms. nitrite (either the pure dry substance or the corresponding amount of moist acid) is heated with 220 gms. of chlorate-free caustic soda and 120 gms. of water in a stirring autoclave during 7 hours at 205–210°, the pressure rising to 14 atmospheres. After cooling and releasing the pressure the contents of the autoclave are diluted up to 1 litre (N.B. the melt should not smell strongly of ammonia), and concentrated sulphuric acid is added until distinctly mineral acid, about 250 gms. conc. sulphuric acid being required for this purpose. After standing a few hours the Gamma-acid is filtered off and well washed with cold water, in which it is very sparingly soluble ; the cake is then pressed and dried at 100°.

250 gms. conc. H_2SO_4.

Yield : About 105 *gms.* (= 95 *gms. of* 100 % *product) Gamma-acid from* " 35 *gms. nitrite," or approximately* 80 % *of theory.* The acid is estimated by coupling with Normal diazotized aniline in dilute strongly alkaline solution, and simultaneously in another sample by diazotizing in very dilute mineral acid solution (for general details as to this type of estimation see Analytical Section). The figures obtained for the two estimations should agree within 1 %, as in the case of H-acid. If the melt has been carried out at too low a temperature the nitrite number will be greater than the coupling figure. The γ-acid should be at least 91 %.

Aminonaphthol Sulphonic Acid 2:5:7 (J-Acid, iso-γ-Acid). M.W. 239.



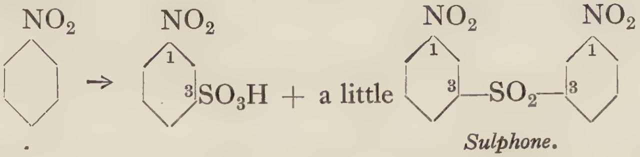
The method is exactly the same as for Gamma-acid, except that preferably somewhat more water is used for the melt, namely 160 gms. instead of 120, and further the temperature is a trifle lower, 200–205° for 7 hours.

The yield is about the same as in the case of γ-acid, i.e. *about* 95 *gms. of* 100 % *aminonaphthol sulphonic acid* 2:5:7 (=circa 105 *gms. at* 92 %) *or* 82 % *of theory.* The yield of 2:5:7-acid is therefore a trifle better than that for γ-acid.

35 gms. Nitrite.
2:5:7-Naphthylamine disulphonic acid. *ca.* 180 gms.
220 gms. NaOH.
160 gms. H_2O.

Nitrobenzene Sulphonic Acid and Metanilic Acid from Nitrobenzene.

Reaction :



1 Gm.-molecule of nitrobenzene is allowed to run cautiously

123 gms. Nitrobenzene. 375 gms. Oleum (25 %).

into three times the quantity of oleum (25 % SO_3) at 70°, contained in a cast-iron pot similar to that used for the sulphonation of the naphthalene sulphonic acid The mixture warms up rapidly to 100–110°, but must not be allowed to rise any higher, or else there is danger of sudden carbonization. When all has been added, the mixture is heated at 110–115° until a test portion poured into water no longer gives any odour of nitrobenzene. If complete sulphonation has not occurred within half an hour of the mixing, then insufficient SO_3 has been used. In this case 50 gms. more oleum are added drop by drop, and if necessary a further quantity after half an hour more, but if the oleum used really contained 25 % SO_3 no more than the original quantity will be required. The mixture is then allowed to cool, and is poured on to 500 gms. ice with good mechanical stirring. The nitrobenzene sulphonic acid goes completely into solution with the exception of a small proportion of sulphone.

500 gms. Ice.

The further working up of the acid may be effected in various ways, *e.g.* as given under H-acid on pp. 15–20. The method recommended is to salt out the acid, as the sodium salt is practically insoluble in saturated brine ; 200 gms. common salt, in small quantities at a time, are slowly sprinkled in with continuous stirring. The sodium salt of nitrobenzene sulphonic acid separates out as a thick paste, and stirring must be continued for some time, until the mass again liquefies. After about 10 hours the solid is filtered off through paper on a large suction funnel, and is then well pressed (in cotton cloth) in a screw-press. The sodium salt can be used technically without further treatment, or may be obtained pure by recrystallizing from water.

200 gms. Salt.

The reduction is carried out as described for H-acid, with the one difference that the iron used need not be subjected to a preliminary "etching," as the free acid contained in the press-cake is sufficient to start the reaction. The reduction product is then neutralized and filtered, as described on p. 18. On evaporating down to 600 c.cs. and acidifying the solution with hydrochloric acid until acid to Congo, the metanilic acid comes out as a finely crystalline precipitate. Many works prefer to use the concentrated solution directly, as the metanilic acid is extremely soluble, and 10–15 % is always lost on separating out, although this loss is more than made up for by the higher yield of finished dye. The *yield* is determined by simply titrating the mineral acid solution with sodium nitrite, and *is about* 90 % = *approximately* 140 *gms. of* 100 % *product.*

250 gms. Iron Powder. 400 c.cs. Water.

ca. 100 c.cs. HCl (30 %), and, if necessary, 100 gms. NaCl.

Other similar Sulphonations.—The following substances are sulphonated in similar manner to the foregoing, *p*-nitro-chlorbenzene, *p*-nitro-toluene, *o*-nitro-chlorbenzene, chlorbenzenes, etc. Dinitro bodies, on the other hand, cannot be sulphonated in this way. Dinitrochlorbenzene, on treatment in this way with fuming sulphuric acid, decomposes with explosive violence, as do the dinitro-toluenes. If it be desired to prepare dinitrochlorbenzene disulphonic acid, for example, one starts with *p*-nitrochlorbenzene: this is sulphonated according to the above method, and the sulphonic acid then converted into the dinitrochlorbenzene sulphonic acid by means of 50 % mixed acid (50 % H_2SO_4+50 % HNO_3) at a low temperature; it has, however, no technical importance. Dinitronaphthalenes are converted into naphthazarine on treatment with oleum.

Notes on Works Technique and Practice.—Sulphonations similar to the foregoing are carried out on the works scale in steam-jacketed vessels through which either steam or cold water may be allowed to flow. The substances frequently heat up very considerably, so that it is necessary to use caution in working, as otherwise dangerous rises in temperature and even explosions may take place. The salting out is done in wooden vats, the pressing of the filter cakes being effected first in filter-presses and then (in hair cloths) in hydraulic presses at 250 atmospheres. The reduction, evaporation, and further working up are carried out as already described.

Sulphanilic Acid.

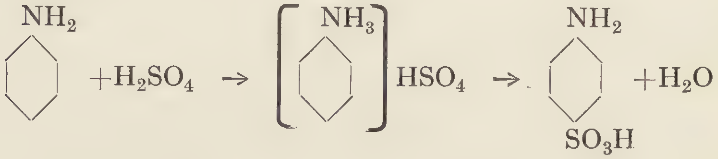
Bake Process.

So far we have only examined cases of sulphonation where the liquid was kept in motion by means of a stirrer. There is, however, another method of sulphonating, which is based on a quite different idea; certain substances sulphonate when their acid sulphates are heated to moderate temperatures. This method obviously applies only to bases, such as aniline, whilst benzidine and more complicated bases, such as dehydro-thiotoluidine, give by this method different isomers from those obtained with the liquid acid.

This reaction is usually referred to as the *Bake Process*, as the acid sulphates are heated on tin trays like baking tins to moderately elevated temperatures.

It is sufficient to heat the dry acid sulphates in thin layers at 170–210° for 5–10 hours in order to obtain practically quantitative yields of the desired sulphonic acids. The most favourable temperature must, of course, be first determined in each case. Again, certain bases, such as benzidine, toluidine, etc., carbonize very easily if any excess of sulphuric acid be taken, particularly in the presence of air ; further, sulphones and disulphonic acids may be formed as well. In modern factories, therefore, the heating is carried out in vacuo, the sulphonation then going more smoothly and more quickly. The ovens used for this reaction are either directly heated with fire, or, better, with superheated steam. Electrical heating may also be employed, and has the advantage of easy regulation, besides avoiding the necessity for using thick boiler-plates.

Reaction :



105 gms.
H_2SO_4,
66° Bé.
93 gms.
Aniline.

Sulphanilic Acid.—105 gms. (=1 gm.-molecule) of 66° Bé. sulphuric acid is mixed with 93 gms. aniline (=1 gm.-molecule) in an iron basin, the base being placed in the vessel and the sulphuric acid added in a thin stream with good stirring. In the factory it is done in an iron pot, and may be worked over with an iron rake. The resultant thick paste is at once spread, whilst still hot, on iron trays (15×15 cms.), furnished with rims 2 cms. deep. The layer should be about 1 cm. thick (8 cms. on the large scale), and the trays are then placed in the drying chest at least 5 cms. from the heating surface, the latter being heated by means of a Bunsen burner fitted with a " mushroom " top ; the mass is heated for 8 hours at 190°. The cakes are then removed from the oven and the resultant sulphanilic acid shaken out of the tin. It is about 90 % pure and pale grey in colour ; in addition to sulphanilic acid it contains about 3 % of unchanged aniline and a little free carbon. For many purposes this crude sulphanilic acid may be used directly by dissolving in sufficient soda to give a strong blue coloration with litmus, in the present case some 60 gms. soda and 500 c.cs. water being required. The liquid is heated to boiling, water being added to balance evaporation, until the steam has removed the easily volatile aniline. It is then run through a cotton filter, and the solution contains a sulphanilic acid which will answer most of the technical requirements without further treatment. In order to obtain pure sulphanilic acid from the solution it is acidified with sulphuric acid until acid to Congo paper. The sulphanilic acid is

60 gms.
Na_2CO_3.
500 gms.
H_2O.

ca. 55 gms.
H_2SO_4,
66° Bé.

precipitated in a very pure form which is, however, not adequate for analytical purposes (*cf*. Analytical portion).

The yield of crude substance is approximately 175 *gms.*, *or about* 140 *gms. of purified reprecipitated acid.*

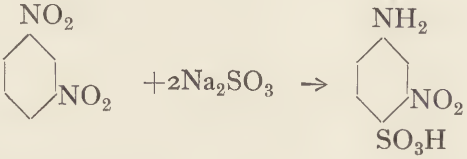
Naphthionic acid (naphthylamine sulphonic acid 1:4) may also be prepared by the baking process in a similar manner. In this case, however, the sulphonation and further working up will not go so smoothly; from 5–10 % of the naphthylamine always remains unchanged but cannot, of course, be removed simply by distilling off with the water as in the case of sulphanilic acid. Further, the unchanged base cannot be removed by filtering the sodium naphthionate solution as the base emulsifies in the solution of the salt and goes through all forms of filter. It is therefore necessary to dissolve the crude acid in alkali and to remove the naphthylamine by treating the alkaline solution with benzene in an extraction apparatus. A further drawback is that a certain quantity (3–7 %) of the 1:5 acid is always produced together with the 1:4 acid. This so-called Laurent's acid can only be removed by crystallizing out the naphthionate, for which reason the naphthionic acid is always dealt with as its sodium salt (naphthionate).

Other Methods of Sulphonation.

In addition to sulphuric acid certain other sulphonating agents may be made use of, although they play no very important part in dye technology. The use of chlor-sulphonic acid as a sulphonating agent will not be discussed here, as it is only employed in very special cases. Its application to the preparation of the acid chlorides of the toluene sulphonic acids may be referred to; these may be prepared in the same apparatus as already described for other sulphonations. In addition to its use for the preparation of sulphonic chlorides chlor-sulphonic acid is still employed for the sulphonation of certain azo colours, as it forms a very mild non-oxidizing sulphonating medium, but it cannot be used for the sulphonation of bases; amino groups inhibit its action at lower temperatures so that it is more advantageous to use sulphuric acid or oleum. Hydroxylated compounds do not yield the sulphonic chlorides of the phenols or naphthols, but give the corresponding free sulphonic acids directly.

Bisulphite and neutral sulphite may also be used under certain conditions for introducing a sulphonic group. This method of introducing a sulphonic group into an aromatic nucleus was first employed by Nietzki (D. R. P. 89097). Thus nitraniline sulphonic acid 3:1:4 may be obtained by the action of sodium sulphite upon dinitro-benzene but in poor yield, and, so far as is known, this is not made use of practically.

Reaction :



More important is the introduction of the sulphonic group by replacing an easily removable chlorine atom with the aid of neutral sodium sulphite, as was proposed by Erdmann in D. R. P. 65240. By a slight modification of this interesting process it is possible to improve the yield considerably.

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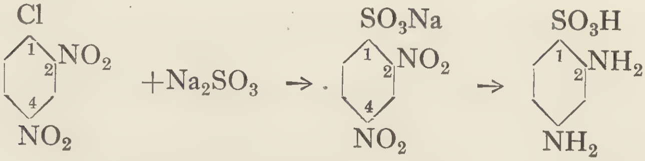
m-Phenylenediamine Sulphonic Acid 1:2:4.

Reaction :



202 gms. Dinitro-chlor-benzene.
500 gms. 90 % Alcohol.
80 gms. SO_2=*ca.* 320 gms. $NaHSO_3$. 25 % SO_2.
ca. 100 gms. 40 % NaOH.

202 Gms. dinitro-chlor-benzene (= 1 molecule) are mixed with 500 gms. of methylated spirits which must not have been denatured with pyridine bases. (Caution is necessary owing to the unpleasant properties of dinitro-chlor-benzene.) To this is added 80 gms. SO_2 (=1 molecule) in the form of a concentrated solution of sodium sulphite. This concentrated solution is prepared from the commercial sodium bisulphite solution by the addition of the exactly equivalent quantity of strong soda lye. 40 % Caustic soda is added until phenolphthalein paper is just faintly reddened. The sulphite separates out to a certain extent even whilst warm, but this is of no consequence. The mixture of dinitro-chlor-benzene, sulphite, water, and spirit is now heated on the water-bath to boiling during 5 hours, with good stirring (Fig. 9, p. 47). The product is then cooled down as far as possible by standing in cold water, when the sodium salt of the dinitro-benzene sulphonic acid separates out in beautiful glistening yellow leaflets,

If the process be carried out exactly in accordance with the patent very unsatisfactory results will be obtained as, according to this, the alcohol is simply distilled off. It is far better to filter off the separated product on a nutsch, and to press out the mass in a screw-press. The leaflets of the sodium salt are then reduced exactly as given for the reduction of dinitro-benzene (*q.v.*). The solution of the *m*-phenylenediamine sulphonic acid is not, however, sufficiently pure for the purposes of the azo colour industry. It is therefore necessary to evaporate down the solution to about 400 c.cs. and to add 100 gms. common salt; on acidifying with hydrochloric acid the free sulphonic acid comes out in fine crystals. It is very important that just the right quantity of acid be taken, as the sulphonic acid will redissolve in any excess; Congo paper should not be turned pure blue, but just a definite faint violet. After two days the product is filtered off and washed in a very little water.

100 gms. $NaCl$.
ca. 100 gms. HCl, 30 %.

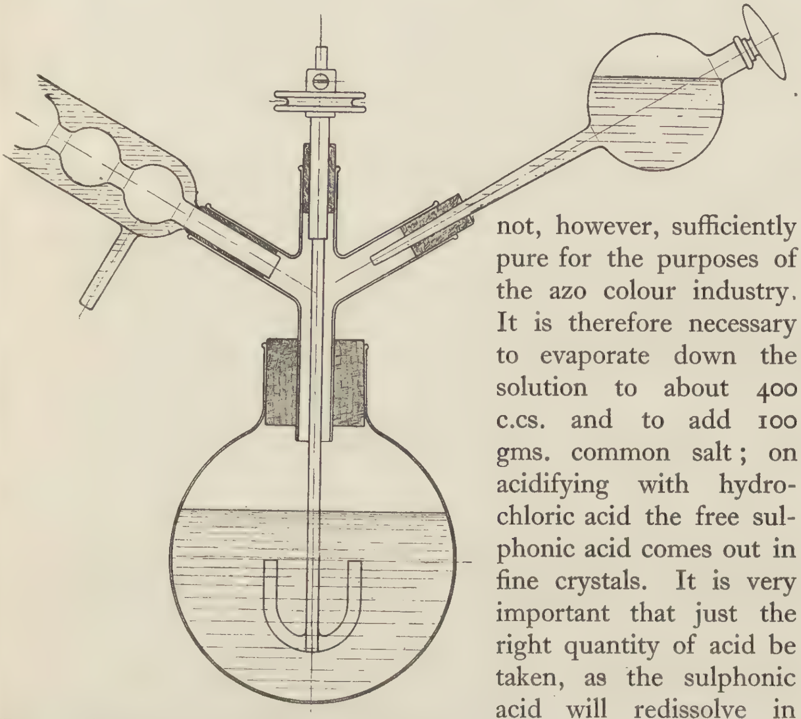


FIG. 9.—Heating under reflux condenser with stirring.

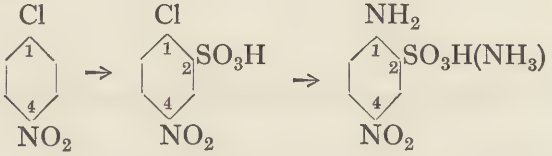
The yield is about 125 *gms. pure substance, or about* 66 % *of theory.*

Notes on Works Practice.—Reactions of this type are best carried out in homogeneously lead-lined iron boilers (*q.v.*). It is very important that no trace of any other metal should come in contact with the liquid. A few milligrams of copper or iron suffice to prevent any trace of the desired compound being obtained. The dinitro-benzene sulphonic acid, as also the finished *m*-phenylene-diamine sulphonic acid, is best not filtered off in a filter-press, but is centrifuged instead. The remainder of the alcohol is removed by hydraulic pressing, and after rectifying in a spirit column, may be used again; with careful working not more than 5 % of the alcohol should be lost during the whole operation.

The mobility of the chlorine atom in negatively substituted aromatic hydrocarbons is frequently made use of for the synthesis of important dye intermediates. Further, actual dyes, particularly those of the anthraquinone series, may be produced by the aid of this reaction. Colouring matters cannot be discussed here in this connection, but a few interesting intermediate products obtained in this manner will now be described.

p-Nitraniline Sulphonic Acid from *p*-Nitro-chlor-benzene.

Reaction:

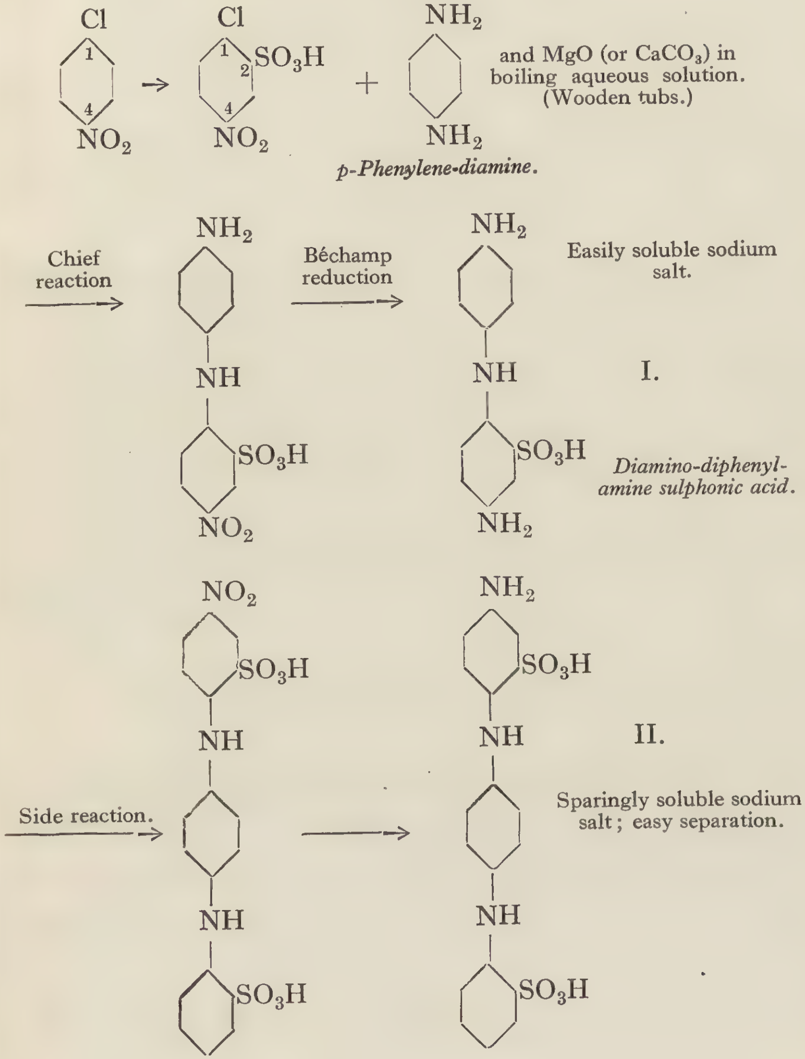


100 gms. *p*-Nitro-chlor-benzene. 100 gms. H_2SO_4, 100 %. 280 gms. Oleum, 25 %.

The sulphonation of *p*-nitro-chlor-benzene is effected in a very similar manner to that of nitro-benzene. Thus, for example, 100 gms. *p*-nitro-chlor-benzene are mixed with 100 gms. of sulphuric acid monohydrate at 50°, and to this are added, with stirring, 280 gms. of oleum containing 25 % SO_3. The product is then warmed to 100–110° until the nitro-chlor-benzene has disappeared. The mixture is poured on to 300 gms. of ice and 300 gms. of water and is salted out with 200 gms. of common salt; after 24 hours the product is filtered off and pressed. *The yield is about* 280 *gms. moist press-cakes.* The cakes are then broken up and heated with their own weight of strong ammonia (20 % NH_3) in autoclaves at 150° during 8 hours, in order to obtain the *p*-nitraniline sulphonic acid. The pressure rises to about 6 atmospheres (steel tube monometer). On cooling, the ammonium salt of the desired sulphonic acid separates out in large, hard, amber-coloured cubes, *which weigh about* 100 *gms. when isolated.* On the large scale the mother-liquor from the ammonium salt is worked up by means of lime to recover the ammonia.

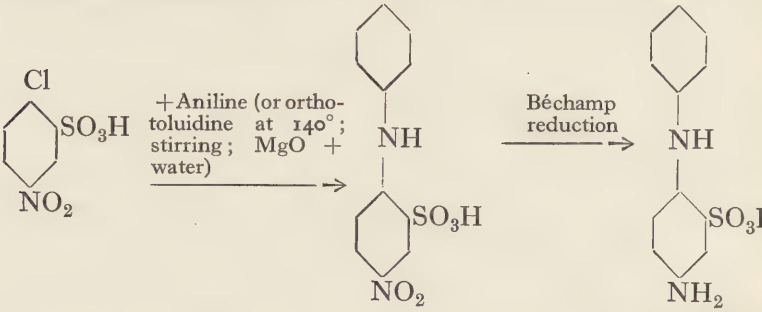
The *p*-nitro-chlor-benzene sulphonic acid finds, in addition, an extensive application in the preparation of diamino-diphenylamine sulphonic acid, and also of amino-diphenylamine sulphonic acid. The following schemes will indicate their modes of formation :

1. *Diamino-diphenylamine sulphonic acid.*


Cl
1
4
NO₂
Cl
1
2
SO₃H
4
NO₂
NH₂
NH₂
and MgO (or CaCO₃) in boiling aqueous solution. (Wooden tubs.)
p-Phenylene-diamine.
Chief reaction
NH₂
NH
SO₃H
NO₂
Béchamp reduction
NH₂
NH
SO₃H
NH₂
Easily soluble sodium salt.
I.
Diamino-diphenyl-amine sulphonic acid.
NO₂
SO₃H
NH
NH
SO₃H
Side reaction.
NH₂
SO₃H
NH
NH
SO₃H
II.
Sparingly soluble sodium salt; easy separation.

The intermediate product (I.) gives valuable dark azo colours for cotton when combined with amino-naphthol sulphonic acids.

2. *Amino-diphenylamine sulphonic acid* (III.) *or amino-phenyl-tolyl amine sulphonic acid.*



III.

Amino-diphenylamine sulphonic acid.

Substances of this type (III.) yield the *Nerols* of the Berlin Aniline Co., which are disazo dyes obtained by coupling with α-naphthylamine and subsequent further coupling with Schäffer salt or with other azo components.

We may note here that not only halogen atoms, but also nitro groups and sulphonic groups may be replaced by phenyl- or aryl-amines. In the anthraquinone molecule in particular the easy replaceability of the nitro groups makes it possible to obtain important derivatives in this manner, but we cannot enter into this question here. The use of various highly nitrated benzene derivatives also gives rise to interesting condensation products.

Preparation of an Amino-naphthol sulphonic acid from the corresponding hydroxy-nitroso compound (Quinone Monoxime):

1:2:4-Amino-naphthol Sulphonic Acid from β-Naphthol.

100 gms. β-Naphthol.
90 gms. NaOH (35 %).
1 litre H_2O.
50 gms. $NaNO_2$.
220 gms. H_2SO_4 (40 %).

1. *Nitroso-β-naphthol.*—100 gms. of β-naphthol[1] are dissolved in 90 gms. of 35 % caustic soda lye and 1 litre of water at 50°, contained in a glass jar of 3 litres capacity. To this solution, which should react faintly but distinctly to thiazole paper, 50 gms. of 100 % sodium nitrite are added, and the mixture made up with water and ice to 2 litres, temperature 0°. About 220 gms. of 40 % sulphuric acid are then allowed to run into this with good stirring during 3 hours; at the end of the time the solution should be distinctly acid to Congo and should react with nitrite paper. After

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[1] A gm.-molecule is not taken as this would need too great a volume of liquid.

10 hours the nitroso-naphthol is filtered off on a big porcelain filter and is well washed. It is chemically pure, assuming that the original β-naphthol was also pure.

2. *Reduction and Conversion into the Amino-naphthol Sulphonic Acid.*—The still moist nitroso-naphthol is stirred up with a little water in a glass jar and cooled down to 5° with ice. To the homogeneous paste is added quickly 260 gms. sodium bisulphite solution (about 25 % SO_2). The nitroso-naphthol goes into solution after a short time, a further small quantity of dilute caustic soda being cautiously added if necessary.

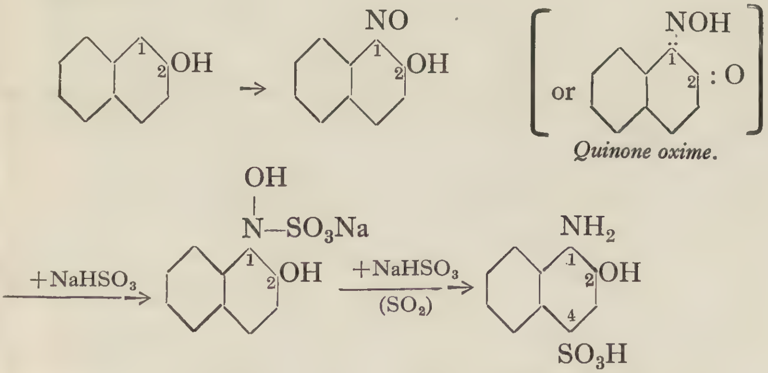
260 gms.
Bisulphite.
(25 %).

The solution contains some resinous constituents, and is therefore filtered. (By salting out the hydroxylamine sulphonic acid which is formed, Alsace Green N or Dioxine N of commerce is obtained, a dye which plays a certain part in calico-printing, the iron lake being very fast to light.)

The volume of the filtered solution is about 1¼ litres. It is placed in a jar and is then treated at 25° with 100 gms. sulphuric acid (66°Bé.) which has been diluted with 200 gms. of water. The solution at the end should show a strongly mineral acid reaction. After 1 hour it is warmed to 50° and allowed to stand overnight; the contents of the jar solidify to a solid cake of free amino-naphthol sulphonic acid. This is filtered off and thoroughly washed out with water. *The yield is about* 90 %, *calculated on the β-naphthol used.*

100 gms.
H_2SO_4,
66° Bé.
200 gms.
H_2O.

Reaction:



Quinone oxime.

"Dioxine." *Amino-naphthol sulphonic acid* 1:2:4.

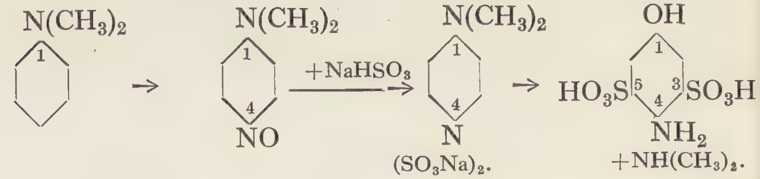
Amino-naphthols of this type cannot be diazotized by the method used for other amines since, on treating with mineral acids and sodium nitrite, quinones are formed and only traces of the desired diazo compound. These diazo bodies, however, may be obtained quantitatively by treating the free acid (as obtained after filtering off and washing) in concentrated suspension with nitrite in presence of a molecule of zinc chloride or of a very small quantity of a copper salt. Both methods are employed, the patent literature giving the essential details (D. R. P. 171024 G.).

Amino-naphthol sulphonic acid 1:2:4 is an intermediate product for important *ortho*-hydroxyazo colours which were discovered simultaneously by Kalle, Geigy, and the B.A.S.F. When coupled with naphthols they yield very fast blue-black chrome dyes ; the nitro derivatives (Sandmeyer-Hagenbach) are the cheapest chrome blacks for wool on the market, and have scarcely been surpassed for fastness (Erio Chrome Black T and A).

It is also of interest to notice that those amines which are substituted in the di-*ortho* positions couple with α-naphthol in the ortho-position to the hydroxyl. Thus from 1:2:4-amino-naphthol sulphonic acid, or, rather, from its diazo compound and strongly alkaline α-naphthol solution, the ortho-hydroxyazo compound is produced quantitatively (Erio Chrome Blue-Black B, Geigy). These diazo compounds are so stable that they can easily be nitrated in sulphuric acid solution by means of " mixed acid " ; the nitro diazo compounds yield the Chrome Blacks mentioned above. Many 2:6 di-substituted anilines also couple with α-naphthol in the ortho position yielding products fast to alkali, whilst from *ortho*-hydroxy diazo compounds and α-naphthol chromable azo colours are formed.

The method of sulphonation by means of sulphurous acid mentioned above, is also applied to the preparation of amino-phenol disulphonic acid from nitroso-dimethyl-aniline and sodium bisulphite. During the conversion to the disulphonic acid, the dimethylamino group is split off leading to the formation of the *p*-aminophenol derivative.

Reaction :



Pure dimethylamine is produced at the same time, which is a commercial product.

PLATE V.

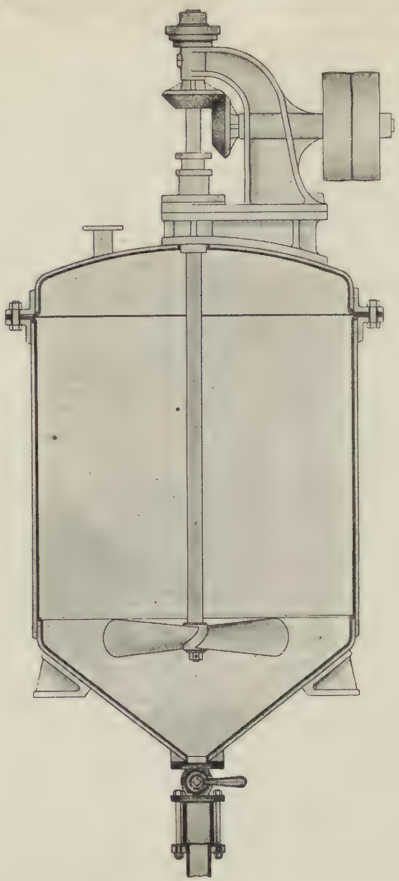


Fig. 12.—Separating funnel and extraction vessel provided with propeller-stirrer and sight-glass (scale 1 : 30).

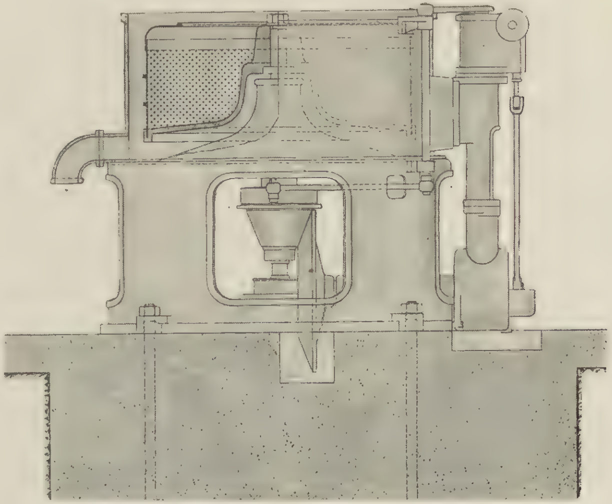
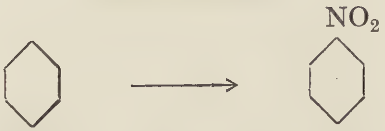


Fig. 13.—Centrifuge with underneath drive (scale 1 : 30).

2. *NITRATIONS AND REDUCTIONS*

Nitrobenzene.[1]

Reaction :



The chief condition to be observed in the manufacture of nitrobenzene is the correct and intimate mixture of the components ; if this is done it is easy to obtain good yields. 100 Gms. of benzene are treated with a mixture of 110 gms. nitric acid (sp. gr. 1·44=44° Bé.) and 170 gms. concentrated sulphuric acid of 66° Bé. with vigorous stirring, in a porcelain beaker provided with a well-fitting lid, or in a glass bolthead (Fig. 9). In order to ensure smooth nitration an acid of sp. gr. 1·46 (=80 % HNO_3=46° Bé.) may be used, but in practice an acid of 1·44 (=75 % HNO_3) is quite sufficient. The internal temperature is maintained at 50° by external cooling, the addition of the acid occupying about half an hour. When all has been added the mixture is stirred for a further 2 hours at 50–60°. The nitrobenzene floats on the surface of the acid, which has a specific gravity of about 1·236. The product is separated in a separating funnel, washed with a little water, then with dilute soda solution, and, finally, again with water. It is then tested with litmus and distilled. At first a little water and some benzene come over, and then pure nitrobenzene. If the benzene used is pure, excellent yields should be obtained even in the laboratory, 100 *gms. of benzene, for example, yielding* 150 *gms. of pure nitrobenzene. B.p.* 205°.

100 gms. Benzene.
110 gms. HNO_3, sp.gr. 1·44.
170 gms. H_2SO_4, 66° Bé.

Notes on Works Technique and Practice.—Nitrobenzene is one of the most important products used in colour technology. It serves for the preparation of aniline and benzidine, and also for the production of the important Nigrosines. On the works scale for the production of nitrobenzene, charges up to 1500 kgs. of benzene are employed, yields of 98 % being obtained. With such large charges the operation lasts about 12 hours, about 97 % of the nitric acid being used up. The course of the reaction is usually followed by a quantitative determination of the amount of nitric acid remaining in the acid mixture. The waste acid should not contain finally more than 1 % of nitric acid (estimation in Lunge nitrometer). The nitrobenzene is usually used without further purification, but to obtain it in a pure condition it is always distilled in vacuo.

Figs. 10 and 11 (Plate IV.) show a nitrating vessel with internal cooling as used for aromatic hydrocarbons, and also a separating funnel with a sight glass (or so-called " lunette ") and a lead or stoneware tap affixed beneath. The nitrating plant for benzene must be homogeneously lead-lined as the waste acid obtained at the end attacks iron owing to its too great dilution.

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[1] Cf. also Ullmann, *Enzyklopädie d. Techn. Wissenschaften.*

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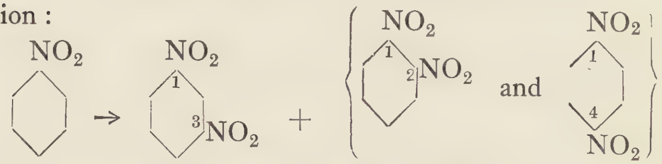
m-Dinitrobenzene from Nitrobenzene.

Reaction :



1:3-Dinitrobenzene, usually referred to simply as dinitrobenzene, is obtained from mono-nitrobenzene. For this purpose the crude nitrobenzene is always employed. It is only necessary to run off the waste acid after the first mono-nitration has been effected. It is not possible to treat benzene straight away with excess of nitric acid as explosions may occur. It is also absolutely essential that the stirring be as vigorous as possible, as insufficient mixing may be extremely dangerous, particularly on the large scale. If, owing to the stopping of the stirrer, two layers should form, consisting of hydrocarbon on the one hand and nitrating acid on the other, the acid should *at once* be run off with the stirrer *stationary*. Cases have been known in the industry where terrible explosions have occurred on subsequently restarting the stirrer owing to sudden overheating (*e.g.* Rummelsburg, near Berlin).

123 gms. Nitrobenzene.
450 gms. H_2SO_4, 66° Bé.
140 gms. HNO_3, 47° Bé.

123 Gms. nitrobenzene are placed in a sulphonating pot of 500 c.cs. capacity. A mixture of 450 gms. concentrated sulphuric acid of 66° Bé. and 140 gms. nitric acid of 47° Be. (sp. gr. 1·48=88 %) is allowed to drop in at 100° during half an hour, with very efficient stirring, which is best effected by means of a propeller stirrer or a Witt's bell-stirrer which must dip right into the liquid. The temperature may be allowed to rise to 115°, and the addition of the acid is so regulated that this temperature is not exceeded. After all has been added, the stirring is preferably continued for a further half-hour. The sulphonating pot is covered with a divided sheet of lead so as to prevent the escape of vapours. The nitration is practically quantitative.

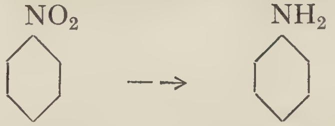
The mixture is then allowed to cool to about 70°, and is poured into half a litre of cold water with good stirring. Some nitrous fumes are evolved (fume cupboard), and the crude dinitrobenzene is at once precipitated as a solid, crumbly mass. The waste acid is decanted off and the residue melted up with about half a litre of water. After cooling and pouring off the washing water, the operation is repeated with the addition of sufficient soda to render the solution strongly alkaline to litmus. Finally, the dinitro product is swirled round at 80° with 500 c.cs. of water, to which 10 c.cs. of 30 % soda lye have been added. A dinitro product is obtained in this way which has a solidifying point of about 80°, and remains practically uncoloured with soda solution ; it is dried in a drying chest at 90°, and, on cooling, a crystalline cake is obtained *weighing about* 150 *gms.*

10 c.cs. NaOH (30 %).

Note on Works Practice.—The technical product is not usually quite so pure as it contains about 3 % *p*-dinitro- and 1 % *o*-dinitrobenzene (see also under *m*-Phenylenediamine). *Dinitrobenzene is an extremely poisonous substance and quite as dangerous as prussic acid.* The workmen who deal with it must always change their clothes in the works and wear gas masks. The substance can even penetrate through the skin into the blood and causes acute *Cyanosis*, a form of poisoning in which the lips of the patient become blue, the pulse weakens, and frequently death supervenes after long illness.

Aniline from Nitrobenzene.

Reaction :



For the preparation of aniline from nitrobenzene we use an autogenously welded iron reaction vessel, such as is shown in Fig. 4 (p. 11).[1] This apparatus is provided with a condenser and dropping funnel, and is charged with 200 gms. iron turnings, 300 c.cs. water, and 20 c.cs. of 30 % hydrochloric acid. The mixture is boiled up for 10 minutes in order to etch the iron. 123 Gms. nitrobenzene are then dropped in during three-quarters hour at the boil, with very vigorous stirring, taking care that the iron is kept continuously swirled up. Considerable heat is evolved, and the nitrobenzene is reduced to aniline, whilst the iron becomes oxidized to Fe_3O_4. Boiling is continued under the reflux until the distillate which runs back down the condenser is colourless. 15 Gms. soda are then added to the reduction liquid and the aniline driven over with steam. The steam is led in through the neck which held the thermometer,

200 gms. Fe.
300 c.cs. H_2O.
20 c.cs. HCl.
1 mol. Nitrobenzene = 123 gms.

15 gms. Na_2CO_3 or CaO.

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[1] A similar apparatus may be used with advantage for sulphonating by means of oleum, as it is unbreakable, and, therefore, quite free from any possible dangers which might attend the use of glass or porcelain pots.

the condenser is fitted to the main opening by means of a bent glass tube, and the third opening is closed up.

Aniline is soluble in water, 100 gms. of water dissolving about 3 gms. of aniline. For this reason enough salt must be added to the aqueous suspension to make a 20 % solution of salt, in which aniline is completely insoluble. After standing for several hours the aniline is run off through a separating funnel and distilled over a naked flame. The first portions contain traces of benzene and a little water, the main fraction coming over at 182° (99 %).

The yield is about 85 gms. aniline from 123 gms. nitrobenzene.

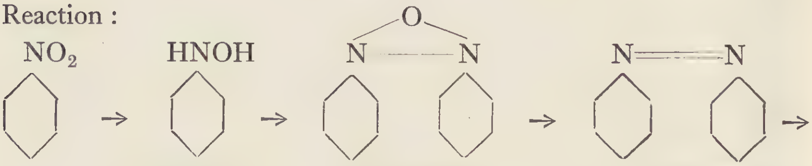
Notes on Works Technique and Practice.—In the works the aniline is distilled over by means of steam which is already saturated with aniline, *i.e.* the boiler is fed with the waste water from the steam distillation. Weiler-ter-Meer, however, simply extract the aniline water with nitrobenzene, the base being completely removed from the liquid by this means. The mixture of nitrobenzene and aniline is then reduced directly as described above. By this means it is possible to avoid the use of boilers charged with aniline water which always cause a certain amount of inconvenience. Fig. 12 (Plate V.) and Fig. 11 (Plate IV.) show the type of apparatus used in the factory.

On the large scale the iron is added gradually and less water is used. The yields obtained are practically quantitative, about 110 kgs. pure aniline being obtained from 100 kgs. benzene. This is distilled in vacuo in quantities of 10,000–30,000 kgs. The heating is always effected by a system of steam pipes fitted inside the still.

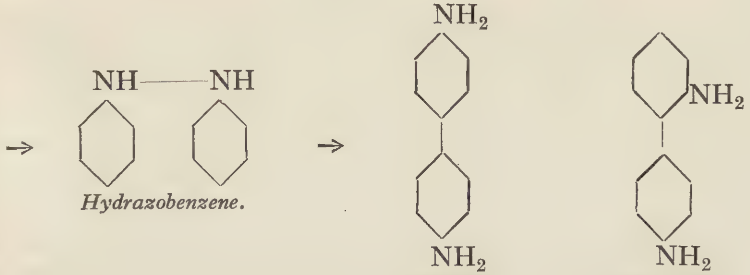
The introduction of the manufacture of aniline gave the first impetus to the development of the colour industry, as aniline has always been one of its most important products. It was first made in England, and at the present time about 50–60 % of the output is utilized for the production of Aniline Black. It may be noted at this point that only a small proportion of the so-called " Aniline Dyes " are actually derivatives of aniline.

Benzidine from Nitrobenzene.

Reaction :



Phenylhydroxylamine. *Azoxybenzene.* *Azobenzene.*



Hydrazobenzene.

Benzidine (*ca.* 85 %).

Diphenyline. (*ca.* 15 %).

Nitrobenzene is reduced to hydrazobenzene by means of cast-iron borings (in strong caustic soda solution), which must have the same properties as the iron used for the Béchamp-Brimmeyr reduction. It is very important to remove all oil from the turnings, or else too much will get into the benzidine. Further, the iron must be very finely divided as only the surface reacts. By the use of soda-lye, water, and iron turnings it is possible to reduce the nitrobenzene step by step and to obtain quantitative yields of hydrazobenzene, though the last stage is a delicate operation. Consequently, a modified process is often adopted as given in D. R. P. 138496 ; this will be referred to later.

The actual laboratory apparatus is illustrated on Plate XIV., Fig. 36. Since the iron turnings offer a considerable resistance to stirring, it is necessary to make use of much stronger apparatus than is usual in the laboratory. It will be found convenient to use a 1 h.p. water turbine or electric motor which can be made to turn a number of driving wheels. On the small scale the thermometer is best left out, owing to its resistance, measurement of the temperature of the oil-bath sufficing.

123 Gms. of nitrobenzene and 30 gms. of 60 % caustic soda solution are first placed in the reduction vessel ; the mixture is then heated to 125° (oil-bath at about 140°). A reflux condenser is provided, as a certain amount of water distils off which carries away some nitrobenzene and reduction products. After the stirrer has been set in motion 400 gms. of very finely divided iron turnings are added during half an hour, which have been previously etched by means of 80 gms. of 60 % soda-lye at 120°. (The alkali attacks the iron with evolution of hydrogen which contains traces of strongly smelling phosphorus compounds ; the etched iron looks like so much damp sand, and on exposing to the atmosphere readily cakes together to solid cement-like lumps, which, on a large scale, may lead to considerable difficulties.)

123 gms. Nitrobenzene.
30 gms. NaOH (60 %).

400 gms. Iron (or 500 gms. if necessary).
80 gms. NaOH (60 %).

300 c.cs. Benzene.

The reduction starts quickly and, after all the iron has been added, is easily completed during 2–3 hours at 125°. Stirring is continued, and the mass allowed to cool. The stirrer must on no account be allowed to stop, or else it will not be possible to start it again. When the temperature has reached 75°, 300 c.cs. benzene are added, and the stirring continued for 5 minutes, the apparatus is then opened, and the solution of azobenzene poured out into a distilling flask. There should be practically no iron in suspension as, with the concentration of caustic soda used, emulsions are rarely formed. The extraction is repeated three times at 75°, by which means the azobenzene will have been completely removed. Care must be taken to avoid the danger of fire.

300 c.cs. Benzene. 50 gms. NaOH (60 %). 200 gms. Fe.

The product may now be reduced directly to hydrazobenzene, but I do not recommend this procedure, as inseparable emulsions are almost always formed, *i.e.* the hydrazobenzene cannot be separated from the iron sludge. If, however, it is desired to use this method, which is that given in the patent referred to, then, instead of extracting, 300 c.cs. of benzene are added, and the temperature kept at 80°. It is also necessary to add a further 50 gms. of caustic soda-lye (60 %), otherwise a hard cement is formed by degrees. To obtain complete reduction a further 200 gms. of iron turnings are added, the end of the reaction being indicated by the benzene solution becoming colourless. The separation of the hydrazobenzene is effected as with the azobenzene.

The azobenzene is obtained completely pure on distilling off the solvent, but before doing this it is necessary to remove all caustic lye by means of carbon dioxide and filtration. *The yield is practically* 100 % *of theory or about* 90 *gms.*

Reduction to Hydrazobenzene.

91 gms. Azobenzene. 250 gms. Alcohol. 200 gms. NaOH (30 %).

220–250 gms. Zinc dust.

100 c.cs. Alcohol (twice).

Reduction by means of Zinc Dust.—91 gms. (=$\frac{1}{2}$ mol.) azobenzene is heated up with 250 gms. alcohol and 200 gms. soda lye (30 % NaOH) to 45° in an iron or glass vessel provided with a powerful stirrer and a reflux condenser. Zinc dust is then added by degrees until the solution is only a faint yellow. According to the purity of the zinc dust, about 200–250 gms. will be required. The temperature during the addition must not be allowed to exceed 60°, otherwise aniline is readily formed. As soon as the liquid has been bleached it is filtered quickly through a nutsch, the zinc dust made into a paste with 100 c.cs. 90 % alcohol, quickly boiled up and filtered into the first portion; the extraction is then repeated. The zinc dust is spontaneously inflammable, and must not, therefore, be thrown into the dustbin.

The aqueous-alcoholic solution separates into two layers, the upper containing the hydrazobenzene, and the lower the sodium zincate. The liquids are run off through a separating-funnel and the upper is saturated with carbon dioxide before evaporating off the alcohol. As much of the alcohol as possible is then distilled off, and 200 c.cs. water are then added to the residue with shaking. The hydrazobenzene comes out first of all as an oil, which then solidifies to coarse crystalline fragments. After filtering off it is quite pure enough for further working up. *The yield of dry substance is quantitative* = *92 gms.*

Modifications.—91 gms. of pure azobenzene are dissolved in 250 c.cs. alcohol, and 250 c.cs of 20 % ammonia are added. A rapid stream of hydrogen sulphide is passed into this suspension, which heats up considerably, becoming darker at first, and then rapidly colourless. The whole reduction occupies about $\frac{1}{2}$–1 hour. On cooling, the hydrazobenzene separates out in beautiful, glistening, colourless or pale-yellow crystals. After standing 12 hours the product is filtered off and washed with a little water. *Yield about* 92 *gms.*

91 gms. Azobenzene.
250 c.cs. Alcohol.
250 c.cs. 20 % NH_3.

This method of preparation has the advantage that no aniline is produced so long as the temperature *does not exceed* 60°, and the hydrogen sulphide is not allowed to act for too long.

Conversion of the Hydrazobenzene to Benzidine.

Owing to the easy oxidizability of the hydrazobenzene it should be dealt with so far as possible in the moist condition. The conversion must be effected by means of hydrochloric acid free from sulphuric acid since benzidine sulphate is insoluble.[1] The finely divided hydrazobenzene is added cautiously to the purified acid. In the present case about 1·2 mol. technical acid (30 % HCl) is used, the liquid at the end of the reaction remaining strongly acid to Congo. The temperature of the transformation is kept as low as possible by the cautious addition of 100 gms. of ice. The hydrazobenzene may be added quickly. The mass is then stirred continuously for 5 hours, and is heated up during 1 hour to 80°, all the benzidine and diphenyline going into solution. At this

ca. 120 gms. HCl (30 %).
100 gms. Ice.

---

[1] Hydrochloric acid, free from sulphuric acid, may be obtained by mixing 15 % commercial acid with barium chloride solution, until no further precipitate is formed.

stage of the operations oily drops of azobenzene frequently form, but only if the temperature has been too high or if much oxidized hydrazobenzene has been used.

The product is now allowed to cool until the precipitate becomes easily filterable, which is usually at about 60°. Where the reduction has been effected by means of ammonium sulphide a fairly heavy precipitate of sulphur is formed which is filtered off warm. The residue is washed out with 50 c.cs. of water at 60°. The solution of the benzidine is always coloured blue- to red-violet. The resultant benzidine hydrochloride is now precipitated with the calculated quantity of sulphuric acid or bisulphate (the cheapest form of sulphuric acid). For this purpose about 55 gms. of 66° Bé. sulphuric acid are required. The benzidine sulphate is precipitated instantaneously as a thick, crystalline deposit. It may therefore be filtered off after a few minutes and thoroughly washed with water containing ½ % sulphuric acid. It is then stirred up afresh with 400 c.cs. of water and made alkaline with about 50 gms. soda. The decomposition of the sulphate must be effected as quickly as possible, as it has been found that after a few hours the salt does not react so rapidly with soda. The benzidine sulphate mother-liquor is deeply coloured, and gives a precipitate of about 8 gms. diphenyline on making alkaline with soda. The free benzidine base, which always becomes a little darker on standing, separates out as a grey-white flocculent mass; it is filtered off and well washed with a little cold water. The dried product has an apparent purity of 98 %, but on distillation about 5 % of the total weight always remains behind in the form of pitch. With very exact working, which is by no means easy to carry out, *a yield is obtained from* 1 *gm.-molecule of nitrobenzene of about* 80 *gms. purest distilled benzidine base* (*B.p.* 405°; 240°/15 *mm.*).

55 gms. H_2SO_4, 66° Bé.

50 gms. Na_2CO_3.

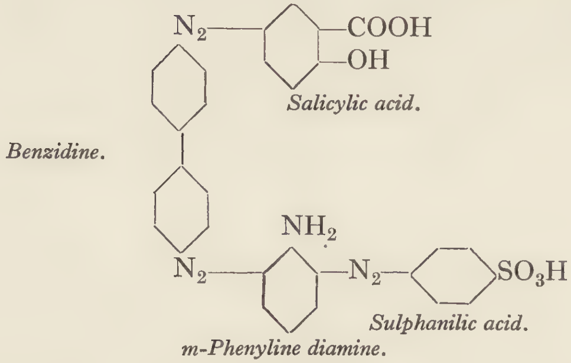
Notes on Works Technique and Practice.—The manufacture of benzidine has developed into one of the most important operations in colour technology, as the direct cotton colours obtained from it are literally indispensable. The price of the product before the war was very low, owing to the keen competition of the different factories, namely about 2 fr. 90 per kilo. Whilst the reduction of nitrobenzene was carried out as recently as 15 years ago exclusively with caustic soda-lye, methyl alcohol, and zinc dust, the situation has altered completely at the present time, as there are now only two processes which can compete. The one which we have discussed replaces these expensive reducing agents by the cheaper iron, which is recovered as iron oxide and can then go back to the blast-furnace. For the last stage of the reduction zinc dust is often made use of in place of iron, but in the works it is more advantageous to complete this stage also by means of iron powder. Once the azobenzene has been isolated, the chief difficulties disappear, as the main bulk of the iron sludge has been got rid of. The reduction of the azobenzene with hydrogen sulphide, however, is also worth consideration as, in certain factories, this is a cheap by-product; it is impossible to say beforehand which process is to be preferred. The quality of the iron must be the same as that used for the Béchamp reduction, and, further, the borings must be carefully freed from grease.

The apparatus used on the works must be built very strongly as the stiff iron mass offers very great resistance to stirring. Plate XI., Fig. 29, illustrates a reaction vessel of this type with duplex stirring gear. In this case the stirrer, however, is made somewhat differently, like a plough, in order that the paddles may go through the iron sludge more easily.

The extraction may be carried out in the reduction vessel itself, the benzene solution being run off through side outlets. Special extraction apparatuses are made also, in which the iron, after separating from the reduction liquor, is extracted. Tip-up vessels, which can be quickly and easily emptied, are sometimes employed. Apparatus of this type is very heavy, but has the advantage over those which are emptied through a bottom exit-tube that it has no spiral conveyor which easily gets stopped up.

Increasing use is being made of centrifuges for separating the mother-liquors from the precipitates, with the exception of the filtration of the benzidine sulphate, which is frequently performed by means of a nutsch (Fig. VI.) or a filter-press. So far no use has been found for the diphenyline obtained as a by-product. Although the 5 % loss on distillation has deterred most factories from isolating the benzidine in this way, I am quite certain, from my own experience, that this loss is apparent rather than real.

The superiority of the distilled benzidine shows itself particularly in the manufacture of complex triazo colours, as in these cases the increased price is more than made up for by the better yields. Colours such as Direct Deep Black E.W. (*q.v.*) or Dianil Brown 3GN, when prepared from quite pure components, will always excel those obtained from less pure materials. It is perhaps hardly necessary to remark that all by-products, such as caustic-lye, unused iron, and solvent should be most carefully recovered.


N₂
COOH
OH
Salicylic acid.
Benzidine.
NH₂
N₂
N₂
SO₃H
Sulphanilic acid.
m-Phenyline diamine.

Dianil Brown 3GN.

Finally, I may mention that the second process, the *electrolytic*, will, in my opinion, gradually displace even the Weiler-ter-Meer process, in spite of all difficulties. It has a great superiority in that absolutely no metal is required, which was a great advantage during the war, when it was extremely difficult to obtain cheap zinc dust. At the present time there is only one factory, and that in Switzerland, which carries out this process successfully.

2:2′-Benzidine Disulphonic Acid from Nitrobenzene.

Reaction :

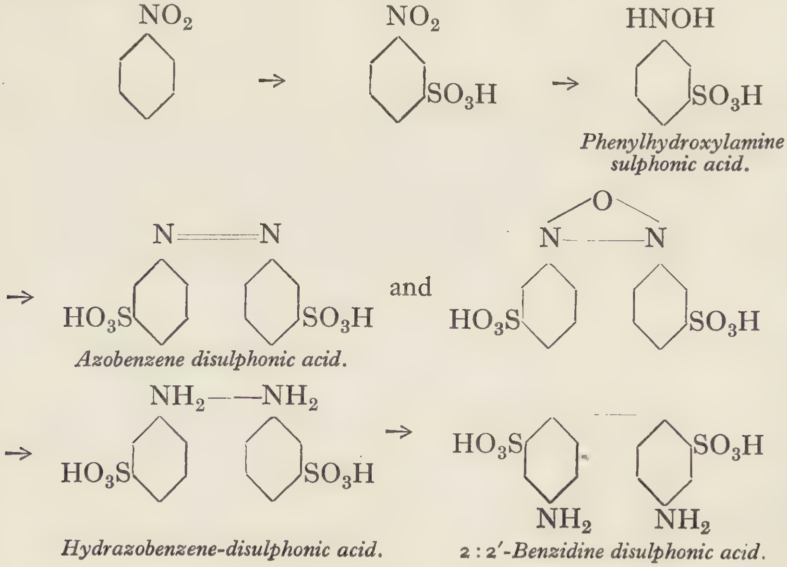

NO₂
NO₂
SO₃H
HNOH
SO₃H
Phenylhydroxylamine sulphonic acid.
N
N
HO₃S
SO₃H
Azobenzene disulphonic acid.
and
O
N
N
HO₃S
SO₃H
NH₂
NH₂
HO₃S
SO₃H
Hydrazobenzene-disulphonic acid.
HO₃S
SO₃H
NH₂
NH₂
2 : 2′-Benzidine disulphonic acid.

PLATE VI.

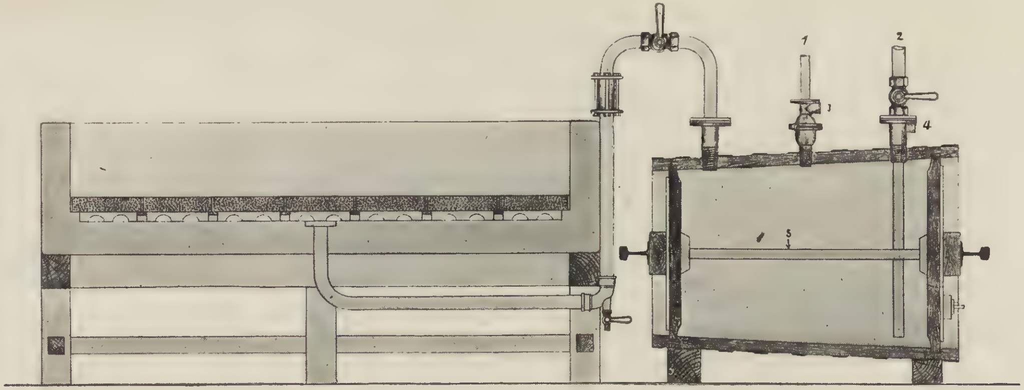


FIG. 14.—Stone vacuum filter for strongly acid precipitates (scale 1 : 30). 1. Vacuum connection. 2. Outlet tube for filtrate. 3. Air by-pass. 4. Connection for emptying out into waste tanks or drains.

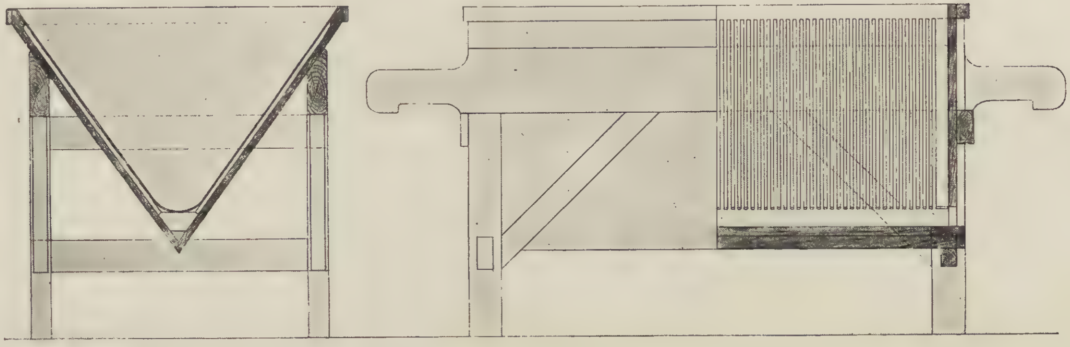


FIG. 15.—Transportable frame-filter for coarsely crystalline precipitates (scale 1 : 25.)

The preparation of nitrobenzene sulphonic acid has been fully described in connection with metanilic acid. The reduction process differs only from similar reactions in that it is carried out purposely in dilute aqueous solution in the present case, and in three stages. It is possible to obtain benzidine disulphonic acid with the use of a minimum quantity of caustic soda and zinc dust.

If the sodium salt used is not quite pure, the press-cakes of sodium nitrobenzene sulphonate corresponding to 100 gms. nitrobenzene are dissolved in about 30 gms. soda so that the solution is exactly neutral to litmus ; it is then made up to $1\frac{1}{2}$ litres at 10°, 10 gms. of ammonium chloride are added, and the liquid vigorously stirred by means of a propeller stirrer. 120 Gms. zinc dust are then added during 2 minutes, a teaspoonful at a time ; finely crushed ice is also added from time to time to keep the temperature below 20°, stirring being continued for 20 minutes. 120 Gms. 30 % caustic soda-lye are poured in quickly, and the mass warmed up to 70° without stirring. The solution, which was originally colourless, at once becomes orange-yellow owing to the formation of the azo- and azoxy-benzene sulphonic acids, and is allowed to stand for at least 3 hours or, better, over-night.

100 gms. Nitrobenzene as sulphonic acid.
1500 c.cs.
NH_4Cl.
120 gms. Zinc dust.
120 gms. NaOH (30 %).

Next day the product is neutralized cautiously by the addition of about 90 gms. concentrated hydrochloric acid, drop by drop, until no reaction is given with thiazole paper. After the liquid has been heated up to 80° a further 40 gms. zinc dust are added. If the colour has not disappeared after 5 minutes, a further quantity of hydrochloric acid is dropped in slowly at 75–80°. The change of colour from a dirty brown to a clear light grey takes place in less than 5 seconds as soon as the neutral point has been reached. The liquid now contains the hydrazine sulphonic acid, its volume being about 1·8 litres, and is quickly run through a filter to prevent further reduction to metanilic acid, the zinc dust being well washed out. After cooling, the filtrate is treated at 20° with 120 c.cs. conc. hydrochloric acid. In a few minutes a glistening precipitate forms, consisting of colourless hard crystals of 2:2′-benzidine disulphonic acid, the liquor becoming yellow through autoxidation ; a few drops of stannous chloride solution are therefore added to decolourize it. Although the benzidine disulphonic acid is extremely sparingly soluble in water (less than 1 gm. per litre), it separates out very slowly, so that the product must be allowed to stand for a couple of days before filtering and washing with cold water.

ca. 90 gms. conc. HCl.
40 gms. Zinc dust.
120 c.cs. conc. HCl.

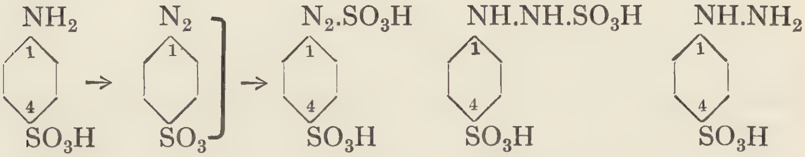
Yield about 65 *gms.*

Notes on Works Technique and Practice.—On the large scale, where one has to deal with volumes of 4000 to 5000 litres, the crystallization of the 2:2′-benzidine disulphonic acid occupies at least 3 days. In order to secure as rapid cooling as possible a leaden coil, through which cold water is circulated, is placed in the wooden tub.

Owing to its insolubility the sulphonic acid must be diazotized indirectly; it is dissolved in the requisite amount of water and soda, the neutral solution mixed with sodium nitrite, and the mixture allowed to run in a thin stream into hydrochloric or sulphuric acid.

Phenylhydrazine Sulphonic Acid from Sulphanilic Acid.

Reaction:



51 gms. Sulphanilic acid.

35 gms. H_2SO_4.

21 gms. $NaNO_2$.

3/10 Gm.-molecule technical sulphanilic acid (100 %) is dissolved in 200 c.cs. water with the aid of 16 gms. of soda, the residual aniline being boiled off with steam. The filtered solution is cooled down in a glass vessel, 35 gms. conc. sulphuric acid are added, and the whole cooled further to 12° (external cooling); it is then treated with a solution of 21 gms. 100 % sodium nitrite in 50 c.cs. water (3/10 gm.-molecule) during half an hour, with continuous stirring, until a distinct and permanent reaction is given with nitrite paper. The diazosulphanilic acid comes out as fine crystals, which are filtered off at 12–14° on a small suction filter. The residue of crystals are rinsed out of the beaker by means of the mother-liquor.[1]

130 gms. $NaHSO_1$ solution.

25–40 gms. NaOH (35 %).

The diazo compound so produced is added to a mixture of 130 gms. sodium bisulphite solution (containing 25 % SO_2), and just enough 35 % caustic soda solution to cause the sulphite to give a distinct reaction with phenolphthalein paper; according to the quality of the technical bisulphite 25–45 gms. soda-lye will be required. If too little be used the hydrazine sulphonic acid becomes discoloured later on and deposits resinous matter. [The use of solid commercial sodium sulphite is unsatisfactory, as its SO_2 content is too variable.] The temperature of the mixture is kept below 50° by placing the vessel in ice water and stirring well. The diazo sulphanilic acid is at once converted into the sulphophenyl-azo-sulphonic acid, which is allowed to stand for an hour.

---

[1] The moist diazosulphanilic acid is quite harmless, but it is highly explosive in the dry state, so that great care must be taken.

It may be converted into the hydrazine sulphonic acid in various ways. The simplest is the following, which is also that used technically. The yellow solution of the azo-sulphonic acid is heated to boiling in a porcelain dish, and the boiling solution treated with 30 % hydrochloric acid (250 gms.) until the reaction is very strongly mineral acid. This operation should take about half an hour, in order to allow the sulphurous acid set free from the neutral sulphite sufficient time to exert its reducing action (fume cupboard !). If the solution should not by then have become decolorized a little more zinc dust may be carefully added. The phenylhydrazine sulphonic acid crystallizes out on cooling and, after standing 12 hours, is filtered off and washed with a little water. *Yield about* 50 *gms.* 100 % product.

ca. 250 gms. 30 % HCl.

The quantitative estimation is carried out by condensing a moderate amount of the substance with aceto-acetic ester in acetic acid solution and weighing the resultant pyrazolone.

Notes on Works Technique and Practice.—The preparation of aryl-hydrazine sulphonic acids has recently gained considerably in importance, as they are the starting-points for various yellow and red colouring matters which are fast to light, certain of which are mentioned later. Most amines of the benzene series may be similarly converted into the corresponding hydrazines ; the chlor-phenyl-hydrazine sulphonic acids and the tolyl-hydrazine sulphonic acids, for instance, are largely manufactured. Certain of them are somewhat difficult to reduce completely, so that the elimination of the sulphonic group attached to the nitrogen atom only takes place at 110–135°. Such sulphonic acids, therefore, are either brought to the necessary temperature in lead-lined autoclaves, or else the difficulty is got over by the following neat device : sulphuric acid is used in place of hydrochloric acid for setting free the sulphurous acid, and is allowed to run under the surface of the boiling liquid. The reaction liquid thereby heats up very strongly and the sulphuric acid hydrolyses the sulphohydrazine sulphonic acid without difficulty ; very occasionally it is necessary to add a little stannous chloride or zinc dust. On the large scale, with ½ kg.-molecule charges, the hydrolysis and reduction occupy about 3 hours. The yields are up to 95 %, and the crystallizations, as in the case of benzidine disulphonic acid, occupy several days.

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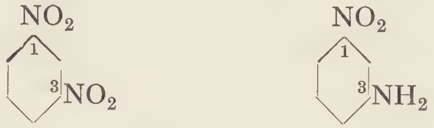
m-Nitraniline from *m*-Dinitro-benzene.

Reaction :



100 gms. Dinitro-benzene.

245 gms Na_2S $+9H_2O$

500 gms Ice.

500 C.cs. of water are heated to 85° in an iron or glass beaker of $1\frac{1}{2}$ litres capacity, 100 gms. dinitro-benzene are then added, and by means of very efficient stirring are practically emulsified (propeller stirrer ; caution required owing to the highly poisonous vapours). 245 Gms. of crystallized sodium sulphide (Na_2S+9 aq.) dissolved in 200 c.cs. of water are then allowed to run into this emulsion from a dropping funnel during 10 minutes. The dinitro-benzene is partially reduced by alkali sulphide, *m*-nitraniline being formed. The end-point of the reaction may be recognized by the fact that a drop of the solution on a filter paper gives a black streak of metallic sulphide with an iron or copper sulphate solution. As soon as the blackening remains for 20 seconds, the mixture is cooled at once to 20° by throwing in 500 gms. of ice, and, after standing for several hours the *m*-nitraniline is filtered off ; it may be recrystallized from boiling water, but for most purposes this is unnecessary. For works use the crude product is simply dissolved in hydrochloric acid, the sulphur filtered off, and the solution utilized directly. *The yield is about* 55 *gms. pure recrystallized* m-*nitraniline.*

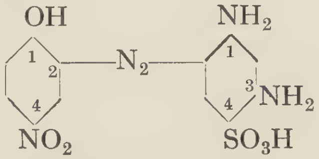
A solution of sulphur and sodium sulphide has also been recommended for the reduction, but this process is not advised, as it leads to poorer yields and less pure products.

It may be noted here that certain nitro compounds cannot be partially reduced in this simple manner, as the reduction for the most part goes too far ; for further details, see the reduction of picric acid to picramic acid (p. 77).

Other nitro compounds must be reduced in ammoniacal solution with exactly the calculated quantity of hydrogen sulphide. It happens frequently that mere careful weighing of the hydrogen sulphide is insufficient, so that it is necessary to make use of various devices. Thus dinitro-phenol can only be satisfactorily reduced to nitro-amino-phenol if it is used in the form of its very finely divided sodium salt, as obtained directly by the hydrolysis of dinitro-chlor-benzene (see Sulphur Black T), which is reduced in ammoniacal solution at about 60° with exactly the calculated quantity of hydrogen sulphide. The nitro-amino-phenol so obtained is then best recrystallized from boiling water.

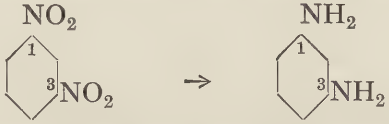
The combination of the sparingly soluble diazo compound with the *m*-phenylene-diamine sulphonic acid, described on p. 46, affords the cheapest chrome-brown on the market. The coupling is effected in a completely neutral solution, and as concentrated as possible, at 28° during 2–3 days.

Chrome Brown R (Kalle) :



m-Phenylene-diamine from *m*-Dinitro-benzene.

Reaction :



For the preparation of *m*-phenylene-diamine the H-acid apparatus shown in Fig. 5 is made use of, and is charged with 168 gms. *m*-dinitro-benzene. As the commercial *m*-dinitro-benzene is not pure it is never possible to obtain yields higher than 90 % of theory. Commercial dinitro-benzene has a melting-point of about 80°, and always contains varying percentages of isomeric products, together, usually, with some dinitrophenol which is easily recognized by the more or less intense yellow colour which it gives on boiling with soda or with caustic soda-lye.

168 gms. Dinitro-benzene.

1½ Litres of water and 300 gms. fine iron turnings are placed in the reduction vessel ; the iron is etched with 20 c.cs. conc. hydrochloric acid, and the mixture heated to boiling for at least 5 minutes. The dinitro-benzene is then added in small portions of not more than 2 gms. at a time with continuous stirring. It will be noticed that the liquid first becomes yellow, due to the formation of *m*-nitraniline ; it froths up on each addition, sometimes so vigorously that it becomes necessary to spray water on to the surface. For the reduction to go properly the temperature must always be kept up to the boiling-point. After every second addition of dinitro-benzene it is necessary to wait until a drop on filter paper is colourless. If the process be hurried too much the liquid becomes brown, due to the formation of azoxy compounds. These prevent the progress of the reduction, which must then be regarded as a failure, and must

300 gms. Fe.

20 c.cs. HCl (30 %).

be stopped. This phenomenon is one of the most undesirable which takes place in any reduction process. It occurs also if poor quality iron be used, for which reason it is most necessary before purchase always to test the samples of iron very carefully as to their activity. With a little practice, however, it is easy to reduce the dinitro-benzene satisfactorily in 40 minutes. At the end a solution is obtained which is frequently either colourless or pale brown and darkens on keeping; it is then boiled for at least 5 minutes, the water which evaporates being replaced so as to keep the volume at about 2 litres, corresponding to a content of about 45 gms. diamine per litre.

ca. 10 gms. Na_2CO_3.

The boiling solution is now treated very carefully with solid calcined soda in small portions (about 10 gms.). As soon as the reaction with litmus is distinct the product is boiled for a further 5 minutes, in order to decompose completely the soluble iron compound of any hydroxylamine which may be present. The liquid should not be filtered until a test on filter paper gives no black stain with sodium sulphide solution (1–10). This test should never be omitted on the large scale, and is likely to save much annoyance.[1] The liquid is then filtered into a bolt-head which has been previously warmed, and the clear filtrate is treated with sufficient hydrochloric acid to cause a slight acid reaction to litmus. A solution of *m*-phenylene-diamine obtained in this manner keeps well. *Yield about* 95 *gms.*, 100 %. The quantitative estimation is carried out in very dilute solution at 0° with diazotized aniline, as in the case of H-acid, except that it is unnecessary to add soda.

This technical solution suffices for many purposes, but a purer diamine is preferable as the final yields are thereby improved. For this purpose the aqueous solution is evaporated first over a naked flame, and then preferably in vacuo, until it contains about 40 % of base; it may now be distilled in vacuo or, more simply, it can be frozen out at 0°. In order to start the crystallization with this "cold" process it is necessary to "seed" the solution with a crystal of phenylenediamine. The purified diamine forms beautiful white prisms containing half a molecule of water, and differs from the impure product in being perfectly stable; *o*- and *p*-diamines are present in the aqueous mother-liquor in concentrated form, which is the reason why the commercial liquor is so easily oxidizable. Orthodiamine gives immediately the characteristic blue-black coloration with aniline, acetic acid, and a little bichromate, by means of which it can be readily identified in the solution.

---

[1] If in spite of long boiling the iron reaction persists, the iron may be precipitated with a little ammonium sulphide.

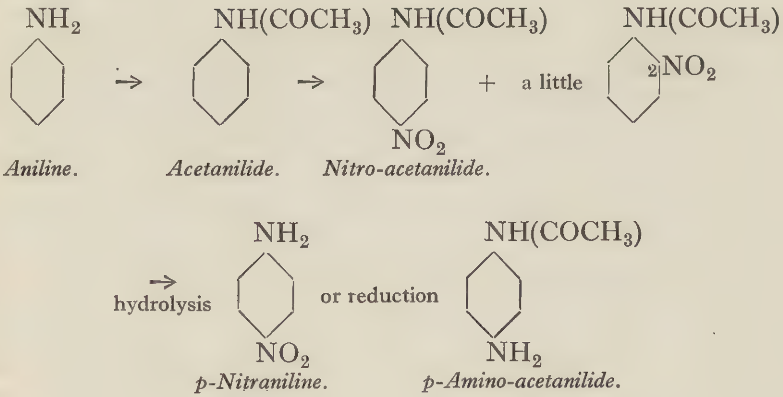
The English firm of Read, Holliday & Sons [1] places a *m*-phenylene-diamine on the market, which has been recrystallized from water, and in spite of its somewhat higher price, it is strongly to be recommended owing to the excellent yields of colour obtained by its use.

The homologous 1:2:4-toluylene-diamine is obtained in a precisely similar manner to *m*-phenylene-diamine. It is characterized by its great purity even in its aqueous solution, as the technical dinitro-toluene is almost chemically pure ; in spite of this, however, it is usually evaporated down and recrystallized in order to obtain a 100 % product. Dinitrochlorbenzene, *p*-nitraniline, and other insoluble nitro compounds behave in a similar manner.

The exceptions, however, are all those compounds containing carboxyl groups (COOH). These cannot be reduced with iron in neutral solution, or only if special precautions be taken, as insoluble iron compounds are immediately formed. For instance, the important nitro-salicylic acid must be reduced by means of tin and hydrochloric acid, the tin being recovered without loss by precipitation with zinc dust. Chlornitro-benzoic acid is best reduced in neutral solution with zinc dust. Nitrophenol sulphonic acids, etc., however, are reduced by means of sodium sulphide (or hydrosulphide) solution under pressure at 120–150°.

p-Nitraniline and *p*-Amino-acetanilide from Aniline.[2]

Reaction :



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[1] This firm is now absorbed in the British Dyestuffs Corporation, Ltd.—F. A. M.

[2] See also, P. Müller, *Ch. Z.* **1912**, 1049, 1055.

Acetanilide.

186 gms.
Aniline.
168 gms.
Glacial
acetic acid.

186 Gms. of purest aniline are heated with the same volume of 100 % (glacial) acetic acid in a bolthead of ½ litre capacity. Highly concentrated acetic acid has a strong action on most metals, for which reason it is necessary to work in glass vessels in the laboratory. The temperature is kept at 130° for ten hours, using a reflux condenser, after which about 25 c.cs. water and acetic acid are distilled off through a Liebig condenser and then a further 50 c.cs. of glacial acetic acid are added. During the second day sufficient water and acetic acid are distilled off for the temperature of the melt to rise to 240°. A further 70 gms. of acetic acid distil over, the strength of the last fraction being over 80 %. The acetylation is now practically quantitative. The acetanilide is poured into a copper tray and the hard melt finely powdered. *Yield about 270 gms. acetanilide.*

50 c.cs.
Glacial
acetic acid.

A still purer product is obtained by stirring the powdered melt with a little water at 70°, after which it is cooled down, filtered off, washed and dried. In this way the last traces of acetic acid are removed. The acetanilide so obtained has a melting-point of 110–111°.

Nitro-acetanilide.

200 gms.
Acetanilide.
800 gms.
H_2SO_4,
66° Bé.

200 Gms. of dry, finely powdered acetanilide are added to 800 gms. concentrated sulphuric acid of 66° Bé., using the apparatus described on p. 5. The temperature should not rise above 25°, as hydrolysis otherwise occurs. The acetanilide dissolves completely to a clear solution in the course of an hour or two. The liquid is now well cooled, and a mixture of 154 gms. nitric acid of 60 % (40° Bé.) and 150 gms. of 92 % sulphuric acid are added during about one hour. The nitrating temperature should not exceed 2–3°, or else rather much orthonitro compound is formed. When all has been added stirring is continued for at least a further three hours, the liquid being preferably allowed to stand all night. A test portion of the mixture on pouring into water and boiling with soda lye should give no odour of aniline.

154 gms.
HNO_3
(60 %).
150 gms.
H_2SO_4,
66° Bé.

500 gms.
Water.
500 gms.
Ice.

The product is now poured, with good stirring, on to 500 gms. of water and 500 gms. of ice. The nitro-acetanilide is at once precipitated, and may be filtered off after an hour without loss. With proper working the theoretical quantity of nitric acid will suffice as is often the case in colour technology. No harm, however, results from a slight excess, as a second nitro group can only be introduced into the molecule with difficulty. The nitro-acetanilide left on the filter is now thoroughly washed with water, then stirred up with a litre of water, sufficient soda added to give a distinct blue colour to litmus paper, and boiled. As a result of this treatment only the *o*-nitro-acetanilide is hydrolysed. The product is filtered at 50° and well washed out with water. *The yield so obtained is about* 90 % *of theory.*

The hydrolysis of the acetyl derivative is always carried out with soda lye; the moist press-cakes of nitro-acetanilide are stirred up with an equal weight of water and the suspension then boiled with 200 gms. of 35 % soda lye. The reaction must remain distinctly alkaline. After about three hours a test portion should give a clear solution in hydrochloric acid, thus indicating complete saponification. The liquor is then cooled to 40° and filtered. The product is carefully washed with cold water and is then chemically pure. *Yield about* 100 *gms. nitraniline from* 93 *gms. aniline.*

Nitro-acetanilide from 200 gms. Acetanilide.

200 gms. NaOH (35 %).

Amino-acetanilide from Nitro-acetanilide.

This azo component is prepared by the neutral reduction of nitro-acetanilde in practically the same way as has already been described several times. In an iron beaker provided with a propeller stirrer are placed 250 gms. cast-iron borings, 15 c.cs. 40 % acetic acid, and 500 c.cs. of water, the whole being then boiled vigorously for a few minutes, after which the moist nitro-acetanilide is added slowly in small portions with continuous stirring and boiling, so that the solution tested on filter paper remains colourless. When all has been added, boiling is continued for a further ten minutes, the evaporated water being replaced. After the liquid has cooled to 70° sufficient soda is added to give a perceptible alkaline reaction. The whole quantity obtained from 93 gms. aniline can easily be reduced in 20 minutes. If boiling be continued whilst neutralizing, or if too much soda be added, the nitro-acetanilide is easily hydrolysed. It is not possible, however, to precipitate at 70° all the iron which has gone into solution, and as this is absolutely necessary the remainder of the metal is precipitated with the minimum quantity of ammonium sulphide until a drop placed on filter paper gives no coloration with alkali sulphide. After this the mass may be filtered.

250 gms. Fe.

15 c.cs. (40 %). Acetic acid.

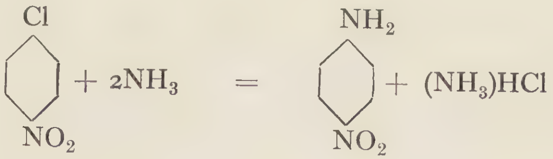
ca. 10 gms. a_2CO_3.

The solution, freed from iron and iron oxide, is now evaporated down to 400 c.cs. over a bare flame. On cooling, the amino-acetanilide separates out in beautiful long needles. *The yield from 93 gms. aniline is about 75 gms. pure base.* The mother-liquor, which always contains about 15 % of less pure products, is evaporated down further after standing for a day, and is then again allowed to crystallize.

The product so obtained is sufficiently pure for the works, but if desired absolutely pure it may be recrystallized from a little water, preferably with the addition of animal charcoal. The solutions, which on the large scale are evaporated down in vacuo, yield a purer amino-acetanilide.

On hydrolysing the amino-acetanilide, exactly as in the case of nitraniline, the important *p*-phenylene-diamine is obtained. It is extremely easily oxidized and is therefore hydrolysed either in complete absence of air, or by boiling with dilute sulphuric acid.

Notes on Works Technique and Practice.—*p*-Nitraniline is one of the most important products of the aniline dye industry. It serves not only for the preparation of solid colours in powder form, but also, and to a still greater extent, for the production of Para Red, which is an azo combination formed on the cotton fibre with *β*-naphthol. The nitraniline is prepared by two different processes ; the most important is that starting from aniline. The manufacture of acetanilide is carried out either in enamel-lined or in aluminium vessels. The mother-liquors are worked up for sodium acetate. The other process starts from *p*-nitro-chlorbenzene, which is converted into nitraniline on heating in an autoclave with ammonia : [1]



Since very high pressures are produced on heating to 200°, many factories fear to use this process, although it gives a *p*-nitraniline which is much purer and just as cheap. For especially pure Para Red, many dyers prefer nitraniline made by this method, which is carried out successfully in certain of the smaller works.

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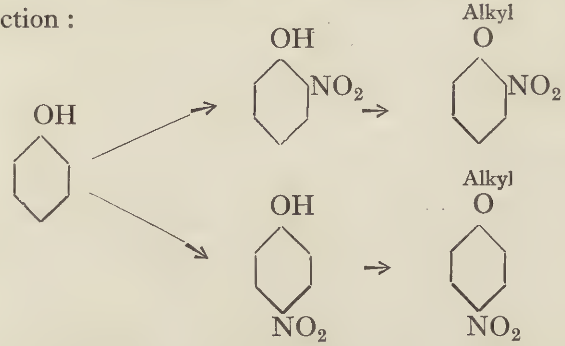
[1] See D. R. P. 148749.

Ortho- and Para-Nitrophenol and their Alkyl Ethers.

Reaction :



93 Gms. Phenol are melted with 20 c.cs. water, and the liquid mixture is allowed to drip into a solution of 150 gms. sodium nitrate in 400 c.cs. of water and 250 gms. concentrated sulphuric acid. During the addition the liquid must be kept well stirred and the temperature below 20°. After all has been added, stirring is continued for a further 2 hours. The mother-liquor is then poured off the resinous mixture of the nitro bodies, and the residue melted with 500 c.cs. of water with the addition of sufficient chalk to give a completely neutral reaction with litmus. The wash-liquor is thrown away and the washing repeated. The crude nitrophenol freed from nitric acid is now steam-distilled, using a wide condenser. About 40 gms. of pure *o*-nitrophenol pass over. The residue left in the flask is then allowed to cool down, and after standing for 24 hours is filtered off from the mother-liquor. The residue is boiled up with 1 litre of 2 % hydrochloric acid and filtered through a folded filter. The pure *p*-nitrophenol crystallizes out from the hot solution in long, practically white needles ; if necessary, the extraction may be repeated.

93 gms. Phenol.
20 c.cs. H_2O.
150 gms. $NaNO_3$.
250 gms. H_2SO_4, 66° Bé.
400 c.cs. H_2O.
$CaCO_3$.

ca. 1000 c.cs. 2 % HCl.

The yield is about 40 *gms. ortho- and about the same quantity of para-derivative.* Treatment of the crude nitrophenol with caustic soda solution has a very harmful effect, although given in various recipes, as the lye has an immediate resinifying action.

Notes on Works Technique and Practice.—In carrying out the distillation on the large scale, either worm condensers standing in warm water, or straight condensers fed with warm water, are used, in order to prevent " freezing up." Preferably the steam is heated to 110° as very little is then required.

o- and *p*-Nitrophenols are the starting-point for the preparation of *o*- and *p*-phenetidine, and for *o*- and *p*-anisidine. From *o*-nitroanisol, further, dianisidine is prepared, which gives the finest direct blue on the market (Diamine Pure Blue, Chicago Blue, etc.).

Alkylation of the Nitrophenols.

Nitrophenols are converted into their ethers by the following general method :—

1 Gm.-molecule of phenol is dissolved in a mixture of 400 c.cs. water, 1 gm.-molecule caustic soda lye, and 80 gms. soda. To this solution are added 500 c.cs. methyl (or ethyl) alcohol of 90 % strength, and it is then cooled to 10°. 1·75 Gm.-molecules methyl chloride or ethyl chloride are then added. The mixture is heated in an autoclave for 8 hours to 100° with stirring or rotation, at 4–5 atmos. The alkylation is then complete ; the product is poured into water, the alkyl ether separated, and the spirit rectified. The alkyl derivative is washed with a little lye and water and should then contain no free nitrophenol.

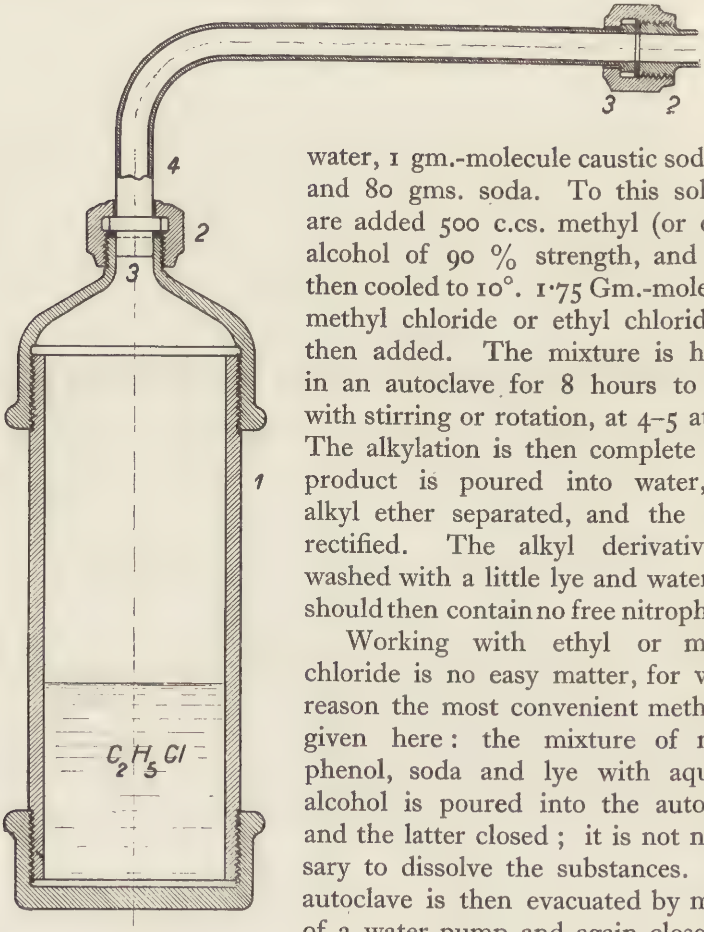


Fig. 16.—Small gas cylinder made of gas-tube for adding alkyl chloride.

Working with ethyl or methyl chloride is no easy matter, for which reason the most convenient method is given here : the mixture of nitrophenol, soda and lye with aqueous alcohol is poured into the autoclave and the latter closed ; it is not necessary to dissolve the substances. The autoclave is then evacuated by means of a water-pump and again closed by means of the valve. A small alkyl chloride bomb made from a piece of gas tube (1) 2 ins. in diameter with a screw nut (3) is then joined on to the autoclave by means of a copper tube (4), and a connection (2), (Fig. 16). The alkyl chloride should previously have been added to the bomb from a cooled glass cylinder, the bomb being placed in ice water for this purpose. As soon as the alkyl-chloride bomb has been attached to the autoclave (I), it is inverted (I*a*) so as to permit the contents to run down the tube. It is now warmed by means of a very hot, wet cloth until one can only just touch it, after which the autoclave valve is opened (Fig. 16A). The warm alkyl-chloride immediately rushes into the evacuated autoclave, the valve of which is closed after a few seconds. It has been shown experimentally that by this means at least 98 % of the alkyl-chloride enters the apparatus. The

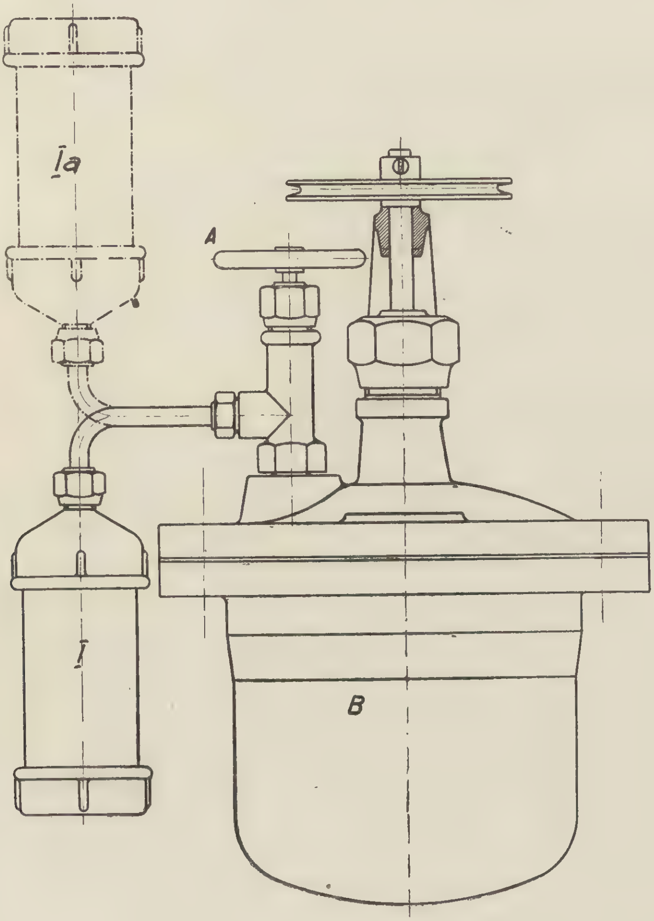


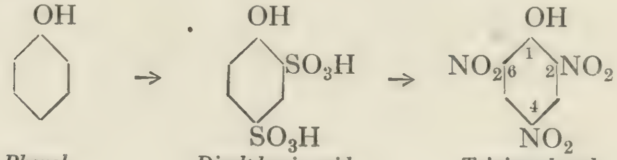
FIG. 16A.—Method of filling a laboratory autoclave with alkyl-chloride.

bomb, which now has no internal pressure, may be removed and the autoclave warmed in an oil-bath as described above.

In the works alkylations are carried out in large horizontal or vertical boilers (see Chrysophenin). The alkyl-chlorides are always prepared from hydrochloric acid, alcohol, and zinc chloride. They are transported in large iron cylinders, and are stored in reservoirs. For use they are filled into steel bottles from which they are either pumped into the reaction vessel, or forced through an inlet tube by means of heat.

Trinitrophenol (Picric Acid).

Reaction :



Phenol. *Disulphonic acid.* *Trinitrophenol.*

93 gms. Phenol. 300 c.cs. H_2SO_4 (100 %).

93 Gms. best quality phenol are placed in a glass, iron, or porcelain sulphonating pot. It is warmed to 100° with stirring, and 300 gms. monohydrate are then added, the temperature being kept below 110°, and maintained at 100–110° for a further hour to ensure the complete sulphonation of all the phenol. The greater portion of the phenol is converted into the disulphonic acid in this manner. By means of external cooling with ice and salt, the contents of the beaker are cooled down to 0°, and to it are added drop-wise during 3 hours, 3·5 molecules nitric acid as 50 % mixed acid.

440 gms. 50 % mixed acid.

Commercial mixed acid is made from very concentrated nitric acid and highly concentrated oleum. Usually nitric acid of sp. gr. 1·48 is mixed with 40 % oleum in large, water-cooled iron kettles. In the laboratory this process is not carried out owing to the great danger. It suffices on the small scale to mix nitric acid of sp. gr. 1·50–1·52 with its own weight of monohydrate.

As soon as all the nitric acid has been dropped into the phenolsulphonic acid, the mixture is allowed to stand over-night at the ordinary temperature, and next day it is warmed very slowly with stirring on the water-bath to 30° during 1 hour. The temperature is then raised to 45°, but no higher, otherwise the mass may suddenly heat up of its own accord ; in this case, even if there is no explosion, all the contents will be forced out of the kettle. The reaction,

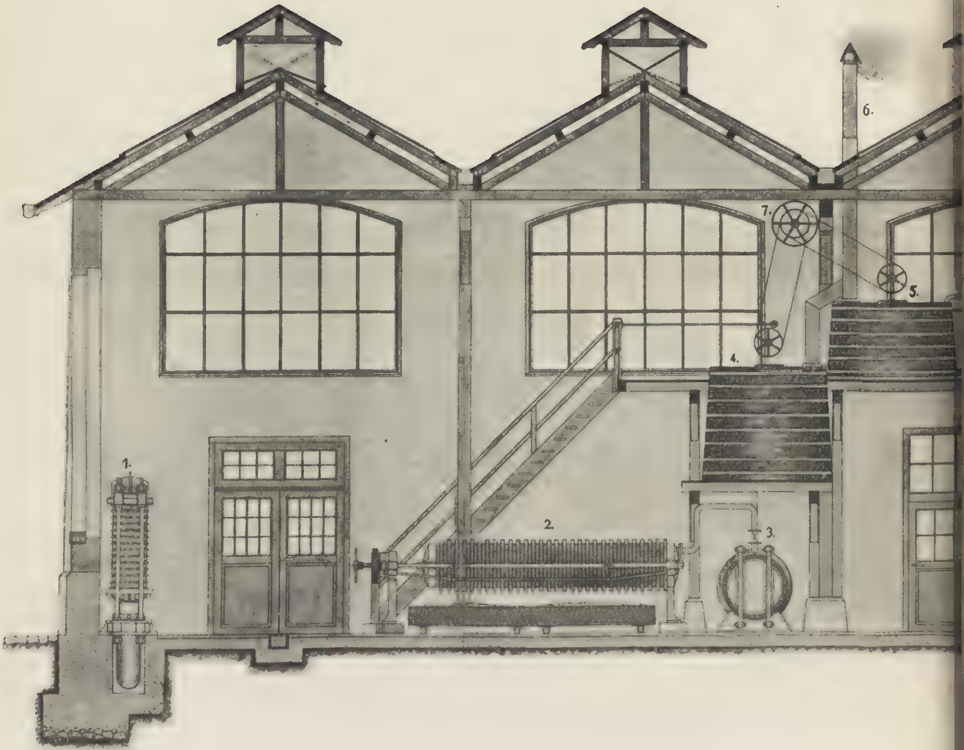
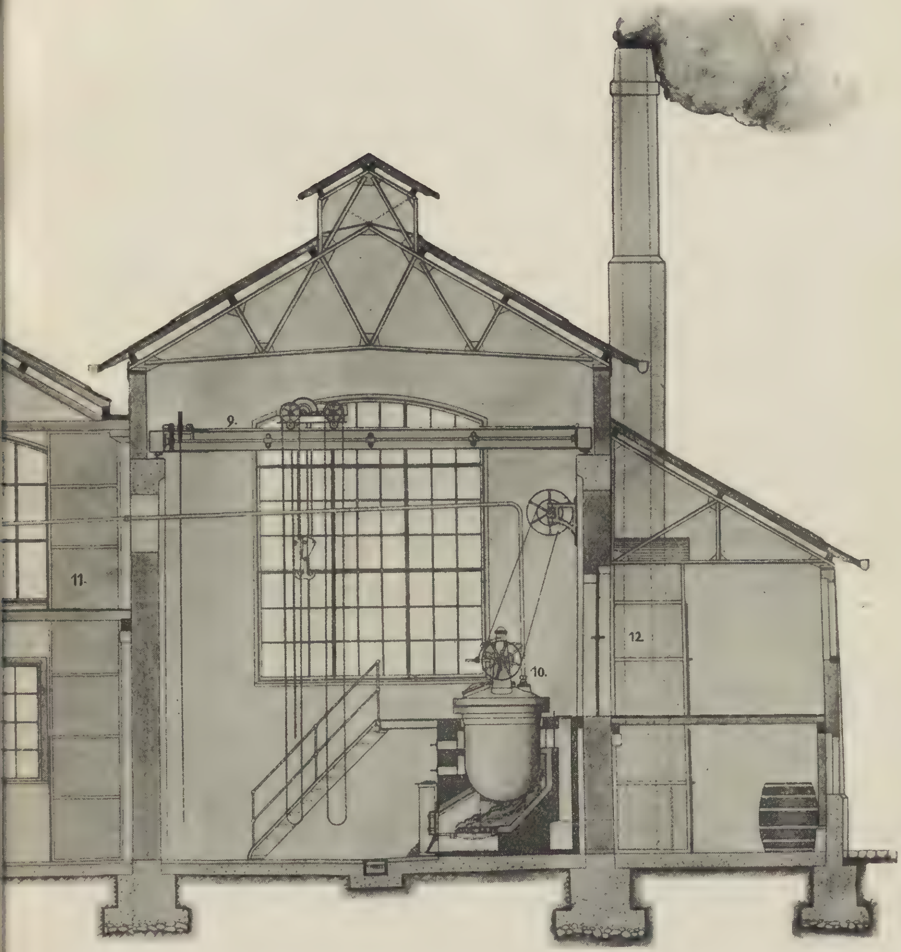


Fig. 20.—General arrangement of a colou

1. Hydraulic press.
2. Filter-press with wooden trays for the filter-cake.
3. Pressure vat with iron supports.
4 and 5. Wooden vats with mechanical stirring gear.

PLATE VII.



in the dye industry (scale 1 : 100).

Ventilating shaft with steam jet.
Driving shaft and wheel.
Pressure pipe from autoclave.
Travelling crane (10 tons).
Autoclave. Capacity 1½ cubic metres.
nd 12. Hoists (3 tons).

however, cannot be completed at 45°. A small portion, therefore, of the nitrating mixture (about 50 c.cs.) is placed in a porcelain dish of $1\frac{1}{2}$ litres capacity and warmed, with stirring, on the sand-bath. The temperature rises rapidly to 110–125°, after which the rest of the mixture is dropped slowly with continuous stirring on to the pre-heated portion, so that no frothing over can take place. The heating is continued for a further half-hour at 110–120°, after which sufficient water is added to produce a sulphuric acid of about 40 %, keeping the temperature at 120°. For this purpose about 700 c.cs. of water are required, as may be easily calculated. Nitrous fumes are evolved, but only in small quantities if the nitration has been properly carried out. The picric acid separates quantitatively on cooling as it is insoluble in 40 % sulphuric acid. A certain amount of resinous and other decomposition products remain in the mother-liquor. The picric acid is filtered, after cooling, through a cotton filter, and is washed with cold water, after which it is chemically pure. *A yield of about* 210 *gms. pure product is obtained.*

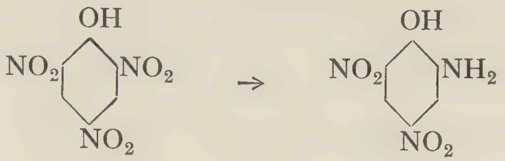
700 c.cs.
Water

In the same way are prepared Martius Yellow (dinitronaphthol 1:2:4), Naphthol Yellow S (dinitronaphthol monosulphonic acid 1:2:4:6), as also dinitro-cresol and other polynitro compounds. With a sufficient concentration of the nitrating mixture, practically the theoretical quantity of nitric acid will suffice.

Notes on Works Technique and Practice.—All the liquids mentioned are strongly acid, and must therefore be filtered through acid-proof material: *e.g.* stone suction filters (Fig. 14, Plate V.), or gun-cotton filter-cloths (nitro-filters). The nitrous gases evolved during the nitration are condensed to nitric acid in towers provided with Raschig-rings.

Picramic Acid.

Reaction :



10 Gms. picric acid and 10 gms. of 35 % soda lye are dissolved in 600 c.cs. water contained in a glass or iron vessel holding at least $1\frac{1}{2}$ litres. After heating up to 55° the liquid is stirred vigorously and a solution of 40 gms. crystallized sodium sulphide and 100 c.cs. water is run in, in a thin stream, during 10 minutes. After the

10 gms.
Picric acid.
10 gms.
36 %
NaOH.
40 gms.
Na_2S
$+9H_2O$.

127·5 gms. Picric acid.
220 gms. $Na_2S + 9H_2O$.
400 gms. Ice.

addition, 127·5 gms. of powdered picric acid are scattered in, about a teaspoonful at a time, a solution of 220 gms. sodium sulphide in 400 c.cs. water being allowed to run in simultaneously during 10 minutes. The addition of the picric acid should end just at the same time as that of the sodium sulphide. If the temperature should exceed 65° a little ice must be added. After all has been added, stirring is continued for a further 10 minutes, after which 400 gms. of ice are added quickly, whereupon the sodium salt of the picramic acid is completely precipitated at once. After standing 10 hours it is filtered off and washed with 10 % brine. The free picramic acid is obtained by stirring up the sodium salt with 500 c.cs. of water, warming to 80°, and acidifying with dilute sulphuric acid until just acid to Congo. After cooling and standing for 10 hours the product is filtered off, *the yield being about* 100 *gms. of* 100 % *product.*

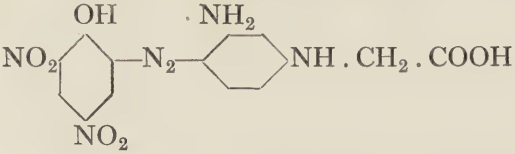
Modification.—The partial reduction of picric acid can, of course, be carried out in various ways. Thus, instead of making the addition gradually and so neutralizing, as it were, the resultant alkali with this acid, the sodium salt may be reduced, the requisite quantity of hydrochloric acid being run in simultaneously.

137·5 gms. Picric acid.
36 gms. Soda.
240 gms. $Na_2S + 9H_2O$.
108 gms. HCl (30 %).
300 c.cs. H_2O.
2000 c.cs. Water.
70 c.cs. 30 % HCl + 400 c.cs. H_2O.

For instance, 6–10 gm.-molecule (=137·5) picric acid are dissolved in 1200 c.cs. water at 50° with the aid of 36 gms. soda; complete solution, however, is not effected. When the carbon dioxide has been driven off, 1 gm.-molecule (=240 gms.) crystallized sodium sulphide dissolved in 450 c.cs. water is run in during half an hour with good stirring. At the same time a mixture of 108 gms., 30 % HCl, and 300 c.cs. water is run in so that the acid takes about a minute longer than the sodium sulphide. After all has been added, stirring is continued for half an hour without heating, the mixture allowed to stand for 12 hours and filtered. The precipitate is washed with 100 c.cs. saturated brine. The crude sodium picramate is dissolved in 2 litres water, and the filtered solution poured into a dilute hydrochloric acid made up of 70 c.cs. of 30 % hydrochloric acid and 400 c.cs. water at 90°. The pure picramic acid is completely precipitated within 24 hours; it is then filtered off and washed with a little water, after which it is pressed and dried at 80°, *the yield being about* 100 *gms.* = 83 % of theory.

On the works scale the former of the two methods given is the more satisfactory, as the gradual addition of the substances can be better regulated.

In recent years picramic acid has become very important as an azo component. It gives very fast wool colours which are distinguished by the fact that they can be dyed with the aid of chromic acid. Examples of these are the Metachrome colours of the Berlin Aniline Co., *e.g.* Metachrome Brown :

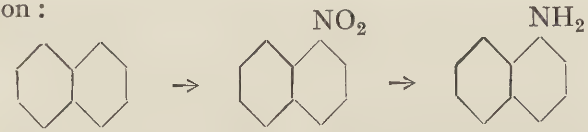


For the most part these dyes are difficultly soluble in water and in the dry state are often explosive, for which reason they must either be ground up with a large quantity of Glauber salt, or placed on the market as aqueous pastes.

The diazo compound of picramic acid was the first example of this class of substances to be discovered, and led to the important researches of Peter Griess.

α-Nitronaphthalene and α-Naphthylamine.[1]

Reaction :



The nitration of naphthalene takes place very vigorously so that poly-nitro products are readily obtained. The naphthalene used should be extremely pure as otherwise the yields are unfavourably influenced. If no satisfactory naphthalene is obtainable, it is advisable to purify some by distillation and, if necessary, by subsequent heating with 5 % of its weight of concentrated sulphuric acid. As the nitration must be performed at a temperature below the melting-point of the naphthalene, the substance must be finely powdered (to pass through a sieve with 400 meshes per sq. cm.), as larger particles would escape the action of the nitric acid.

128 Gms. naphthalene are added to a mixture of 103 gms. nitric acid of 60 % (40° Bé.), and 300 gms. of 80 % sulphuric acid. Stirring is continued without interruption for 6 hours at 50°, the temperature being finally increased to 60° during 1 hour, after which it is cooled down. The nitronaphthalene floats upon the surface of the acid in porous cakes, and consists of about 95 % α-nitro compound, together with some unchanged naphthalene and a very little dinitro derivative. β-Nitronaphthalene is either absent or present only in traces.

128 gms. Naphthalene.
103 gms. HNO_3, 40° Bé.
300 gms. H_2SO_4 80 %.

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[1] See also O. N. Witt, *Chem. Ind.* (1887), 215 ; S. Paul, *Z. f. a. Ch.* (1897), 145.

The crude product is melted up several times with boiling water by which means the acid is completely removed and the naphthalene carried off by the steam. The melted product is then poured into cold water, which is kept well agitated, the nitronaphthalene separating out in the form of small spheres.

To obtain the compound completely pure, it is dried by melting it at 120° in an air oven. It is then treated with 10 % of its weight of ligroïn (b.p. about 150°), or crude xylene or cymene may be used instead. It is then filtered hot through a smooth filter and allowed to stand in a closed vessel for some time. A crystalline cake is formed which is well pressed out in a cotton cloth. This purification should be repeated until the nitronaphthalene shows a melting-point of 61°. It is thus obtained in the form of yellow, glistening crystals. A considerable portion of the nitronaphthalene always remains behind in the mother-liquors and may be recovered by distilling off the solvent.

Crude nitronaphthalene is reduced by Béchamp's method by means of iron and a little hydrochloric acid ; the mixture must not, however, be heated too high or else too much naphthalene will be formed ; but it is not possible to prevent this reaction altogether, as, for instance, in the preparation of aniline, although in the latter case its effect is but slight.

200 gms. Fe.
100 gms. H_2O.
10 c.cs. 30 % HCl.
173 gms. Nitronaphthalene.

200 Gms. iron turnings, 100 gms. water, and 10 c.cs. of 30 % hydrochloric acid are placed in an iron reducing pot, fitted with an " anchor " stirrer. As soon as the evolution of hydrogen has ceased at 50° the nitronaphthalene is added in small portions, taking care, by means of external cooling, that the temperature rises no higher. One gm.-molecule (=173 gms.) nitronaphthalene (calculated as air-dried substance) is reduced within 4 hours, with continuous stirring. It is inadvisable to proceed more quickly or undesired azo compounds may be formed. The mixture is now treated with enough soda to give a distinctly alkaline reaction, after which the contents of the reduction vessel are transferred to a basin. The separation of the α-naphthylamine formed is best effected even in the laboratory by distilling with super-heated steam, for which purpose the whole reduction product together with water, iron, and iron oxide are placed in the oil-heated pot shown in Fig. 36, Plate XIV. The water is distilled off completely with continuous stirring by heating the oil-bath to 200°, after which super-heated steam at 250° is blown in (Fig. 17).[1]

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[1] The illustration is diagrammatic and does not show the stirrer. In order to ensure the easy separation of the iron oxide and naphthylamine, it is advisable for the mixture to be kept stirred.

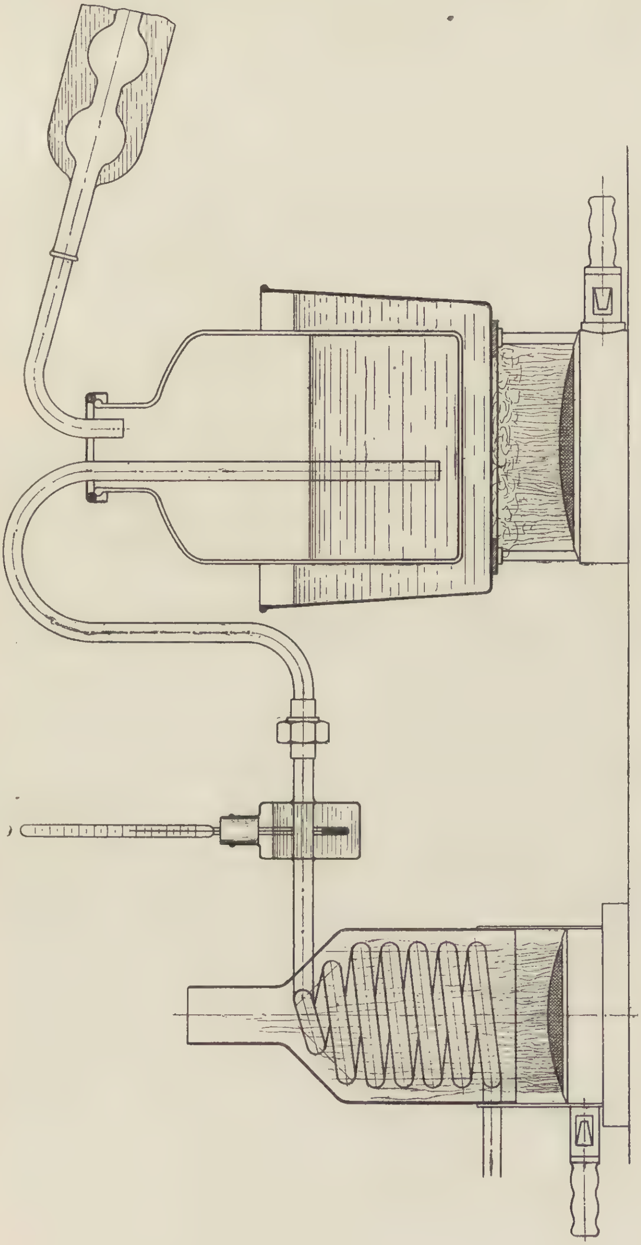
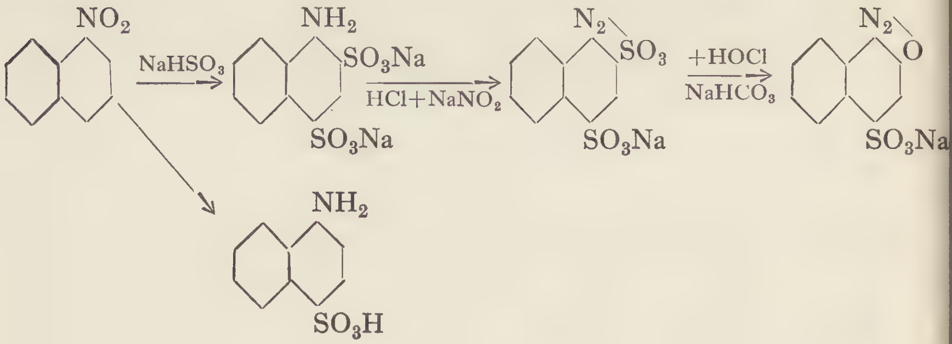


Fig. 17.—Apparatus for distilling in a current of superheated steam.

If the distillation is carried out properly, it is possible to distil over half to one part naphthylamine for each part water. A small amount of finely divided iron powder, graphite from the cast-iron, and iron oxide, are always carried over with the base. As soon as the point is reached at which the steam at 260° carries over only discoloured products or none at all, the distillation is complete; it should occupy from 1–1½ hours according to the method of heating. There remains in the kettle a black very finely divided mass, which is pyrophorous, and therefore must not simply be thrown away. After cooling, the naphthylamine is separated from the mother-liquor, melted, and dried at 110° in the air oven, after which it is vacuum-distilled. The base is obtained as a completely colourless crystalline product. *The yield from* 1 *gm.-molecule of naphthalene is about* 110 *gms. pure α-naphthylamine. M.p.* 50°.

Notes on Works Practice.—(*a*) Nitronaphthalene. A portion of the waste nitrating acid is always made use of again by simply making up to 80 % by the addition of stronger sulphuric acid. The residue is used for acidifying alkali melts, etc. With correct grinding (disintegration at 60°) it is possible to obtain practically quantitative yields in the nitration. The nitronaphthalene is also used for the preparation of 1:5-nitronaphthalene and 1:5 naphthylamine sulphonic acids. Further, the nitronaphthalene has been applied (first by the B.A.S.F.) to the preparation of the diazo compound of aminonaphthol sulphonic acid 1:2:4; on heating with sodium sulphite it yields naphthylamine disulphonic acid 1:2:4, together with some naphthionic acid; the former can be diazotized and converted into the diazo compound of the above mentioned sulphonic acid on treatment with sodium bicarbonate and sodium hypochlorite. The following scheme illustrates the course of this curious reaction (see D. R. P. 160536):



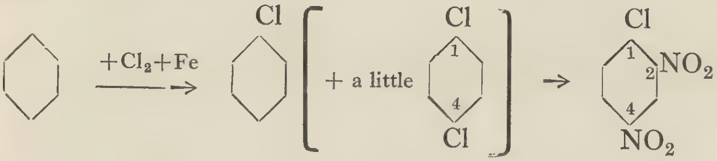
Although this process is quite satisfactory it has been replaced by the still cheaper Sandmeyer method.

(*b*) α-Naphthylamine. The reduction is carried out in a similar apparatus to that which has already been described on several occasions. But owing to the stiff, porridgy consistency of the reduction liquid, it is not possible to use a plough- or propeller-stirrer, but the " anchor " type must be utilized, such as that given in Plate II. The steam distillation is effected in an apparatus similar to that indicated in Fig. 19. The incoming steam is almost invariably pre-heated in a special superheater. Satisfactory apparatus of this type is supplied by various makers.

3. *CHLORINATIONS*

Chlorbenzene and Dinitrochlorbenzene from Benzene.

Reaction :



On the works scale the introduction of chlorine and bromine into aromatic hydrocarbons is carried out almost exclusively by direct halogenation. Only in very special cases is the Sandmeyer reaction used, as, for instance, in the case of the chlorbenzaldehydes, for which purpose the pure chlortoluenes are best made from the corresponding toluidines (see p. 91).

Benzene readily takes up chlorine in the presence of carriers ; iron is the only catalyst of practical importance. In this case the best iron for the purpose is not cast-iron, but wrought-iron, as it acts less vigorously.

600 Gms. of pure dry benzene are heated to boiling with 5 gms. of wrought-iron powder in a litre bolthead fitted with a reflux condenser ; a slow stream of dry chlorine is then passed through at 79° with vigorous stirring (Figs. 18 and 18A). The chlorine must always be carefully dried by means of at least three wash-bottles [1]

600 gms. Benzene.
5 gms. Fe.

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[1] The so-called " Spiral " wash-bottles, in which the gas bubbles are compelled to follow a long spiral course through the sulphuric acid, are strongly recommended.

and a calcium chloride tube, as any trace of moisture encourages side reactions.

The hydrochloric acid evolved during the addition is led into a flask containing a layer of water which absorbs the hydrochloric acid gas practically completely. The inlet tube should not touch the surface of the liquid or else the water will be immediately sucked back into the chlorinating flask. Chlorine is passed in until about 90 % of the calculated quantity has been used up. If an excess be used too much dichlorbenzene is produced, which hitherto has found use only as a moth-preventive. The chlorination of 600 gms. benzene lasts about 5 hours and, altogether, sufficient chlorine should be used to cause an increase in weight of 260 gms.; the gas must not be passed in too rapidly or else too much benzene will be carried off, which must be allowed for in the calculation. If the inlet tube should become stopped up with dichlorbenzene, the

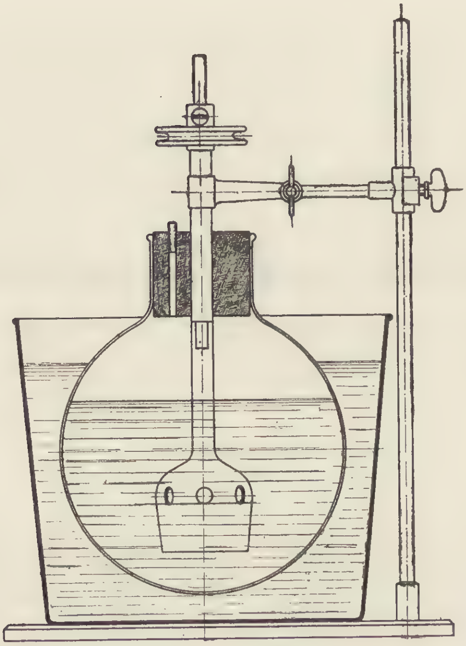

FIG. 18.—Stirring by means of Witt's bell-stirrer.

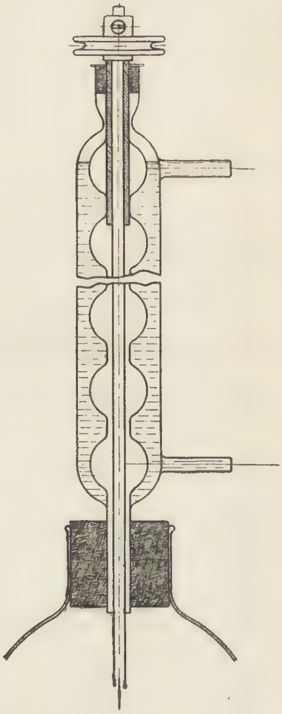

FIG. 18A.—Heating under a reflux condenser, and stirring, with an ordinary bulb condenser.

260 gms. increase in weight = 520 gms. Chlorine.

stream of chlorine is interrupted for a short time, when the dichlor product will rapidly dissolve again.

When the chlorination is complete, the product is allowed to stand for some time and is then poured off from the iron sludge. The mixture is rectified by means of a fractionating column at least 30 cms. long, filled with glass beads. Approximately the following fractions will be obtained :—

B.P.	%	Composition.
79–81°	3	Benzene.
81–125°	10	Benzene and Chlorbenzene.
126–133°	85	Chlorbenzene.
133–180°	5	Chlorbenzene and Dichlorbenzene.
—	5	Resinous matters and loss.

The fraction boiling at 126–133° is re-distilled through the column, 700 *gms. of pure chlorbenzene of b.p.* 131–132° *being finally obtained. The yield, calculated on the benzene actually used up, is about* 90 %.

Notes on Works Practice.—Chlorbenzene has become an important intermediate for various other compounds (*cf.* dinitrochlorbenzene). It is produced in quantities of 2 tons or more at a time, in cast-iron vessels provided with stirring gear and reflux condenser. The rectification is carried out very carefully, the *Kubierschky* columns coming more and more into use for this purpose, as they are far more efficient than the older types. The vapours run through the entire length of the column almost without resistance, and are thoroughly washed out ("dephlegmated") by the descending current of liquid. Other forms of column are also used such as the cheap and effective *Raschig* column, in which the gases pass through a tower filled with short cylinders possessing the same height and diameter. These rings therefore lie quite irregularly in the tower, and give a large surface without offering much resistance. Plate IX. shows rectifying columns of these types which can also be erected for continuous service. It is possible to effect the separation so completely that the yield of pure distillate, calculated upon the benzene used, rises to 96 %. The hydrochloric acid evolved in such chlorinations is condensed in the well-known stoneware Woulf bottles. The small amount of chlorine present is neutralized by the addition of a little sodium bisulphite. This "chlorination-hydrochloric acid" is cheap and very pure, and plays an important rôle in the colour factories.

Dinitrochlorbenzene from Chlorbenzene.

The nitration of chlorbenzene takes place very readily; it is nitrated first only to the mono-nitro stage, as given under the preparation of dinitrobenzene. The product is a mixture of ortho- and para-derivatives which is not easy to separate as their boiling-points are very close to one another, namely, 243° and 242° for the ortho- and para- compounds respectively.

For this reason the separation is always effected by freezing out, centrifuging and distilling in vacuo with a very tall column. This operation cannot be properly carried out in the laboratory, but it is quite easy to separate a large portion of the para product in a pure condition from the crude mixture of the two nitrochlorbenzenes by freezing out and pressing. The nitrochlorbenzenes are very poisonous, for which reason the centrifuges in which the product is "whizzed" must be very carefully built, provided with well-fitting covers with flues similar to those in which, for instance, gun-cotton is dehydrated by means of alcohol.

We will therefore not discuss the preparation of the mono-nitro compounds, but will proceed directly with the further nitration of the mixture.

350 gms. mixed acid (50 % HNO_3).

113 gms. Chlorbenzene.

350 gms. conc. H_2SO_4 (66° Bé.).

350 Gms. of mixed acid containing 50 % HNO_3 are placed in an iron nitrating vessel (Fig. 2), and into this is dropped 113 gms. chlorbenzene with good stirring, keeping the temperature below 5°. After all has been added the stirring is continued for a further hour at 5–10°. The temperature is then raised slowly to 50°, and kept for a further hour at this temperature. 350 Gms. concentrated sulphuric acid are then dropped in very cautiously with continued vigorous stirring, the mixture being finally heated for half an hour at 115°. After cooling, the nitrated product is poured into 2 litres of water, in which it immediately solidifies to a pale yellow cake. This is separated from the mother-liquor, melted under water to remove all acid, and is then chemically pure.[1]

The yield is 200 *gms. from* 113 *gms. chlorbenzene. M.p.* 51°.

Notes on Works Technique and Practice.—The manufacture of dinitrochlorbenzene has assumed quite unexpected proportions. It serves for the preparation of Sulphur Black T (*q.v.*) and other important dyes. Further, it is the starting-point for a whole series of condensation products which are obtained by replacing the mobile chlorine atom by basic and other radicals. Thus, for instance, hexanitrodiphenylamine is obtained from it, which is one of the most powerful of present-day explosives (torpedoes).[1] Further, dinitraniline, dinitrophenol, and picric acid can be readily obtained from it. The diagram given below shows only a small portion of the various practical possibilities.

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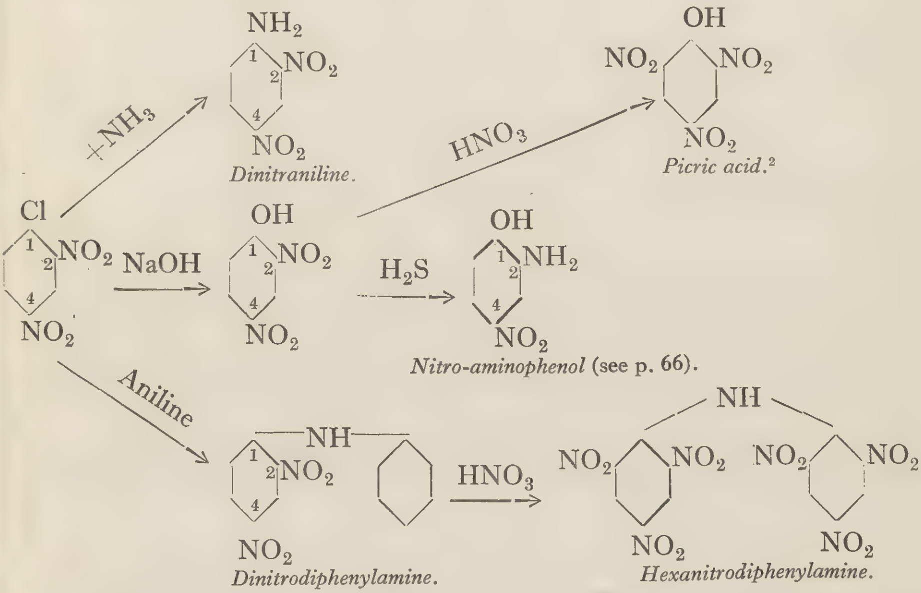
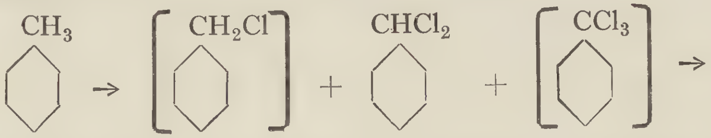
[1] It is advisable to offer a word of warning as to the extremely unpleasant properties of dinitrochlorbenzene. Both as a solid and, more especially, in its solutions it produces eczema and unbearable itching.


NH₂
NO₂
NO₂
Dinitraniline.
+NH₃
OH
NO₂
NO₂
NO₂
Picric acid.[2]
HNO₃
Cl
NO₂
NO₂
NaOH
OH
NO₂
NO₂
H₂S
OH
NH₂
NO₂
Nitro-aminophenol (see p. 66).
Aniline
NH
NO₂
NO₂
Dinitrodiphenylamine.
HNO₃
NH
NO₂
NO₂
NO₂
NO₂
NO₂
NO₂
Hexanitrodiphenylamine.

We have seen that in the laboratory a 30 % excess of nitric acid is used in order to obtain smoother nitration. On the large scale it is possible to manage with a much smaller excess, and even this is finally recovered by separating the waste acid into sulphuric and nitric acids in denitrating towers by means of steam. Dinitrochlorbenzene costs less than 90 centimes per kilo.

Benzalchloride and Benzaldehyde from Toluene.

Reaction :


CH₃
CH₂Cl
CHCl₂
CCl₃

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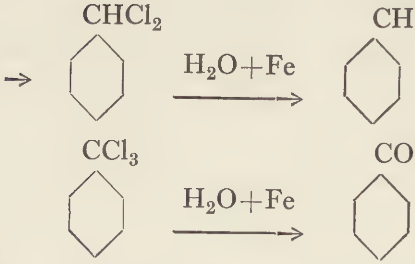
[1] For manufacture, cf. *Zeitschr. f. das Gesamte Spreng und Schiesswesen* (1913), **8**, 205 and 251 (Carter).

[2] Picric acid may also be prepared *via* picryl chloride.



Benzaldehyde.

Benzoic acid.

455 gms. Toluene. 10 gms. PCl_5. 355 gms. Chlorine (increase in weight).

Benzalchloride.—455 Gms. (=5 mols.) dry toluene and 10 gms. phosphorus pentachloride are heated to boiling in a 1-litre bolthead provided with stirrer and reflux condenser, and dry chlorine is passed in until the increase in weight is 355 gms.[1]

This takes about 6 hours. The resultant mixture of unchanged toluene, benzyl-, benzal- and benzotri-chlorides is rectified with a glass-bead column and the fraction between 160 and 225° collected separately. Its chief component is benzalchloride, boiling at 204°, together with a little benzylchloride and benzotrichloride. In the factory it is possible to separate these components satisfactorily by careful fractionation.

Benzaldehyde.—The benzalchloride used for the preparation of benzaldehyde must be free from benzylchloride, and must therefore first be very carefully rectified, the portion passing over below 180° being rejected.

161 gms. $C_6H_5.CHCl_2$. 0·5 gm. Fe. 25 gms. H_2O. About 20 gms. Na_2CO_3. About 300 gms. $NaHSO_3$ (25 % SO_2).

161 Gms. (=1 mol.) benzalchloride containing a little benzotrichloride is heated to 30° in a small glass bolthead with $\frac{1}{2}$ gm. iron powder during half an hour, with stirring. 25 C.cs. water are then added and the mixture heated cautiously until evolution of hydrochloric acid begins (at about 100°). The reaction now proceeds by itself for a certain length of time, and is completed by gentle warming. Sufficient soda is then added to turn litmus blue and the benzaldehyde is distilled over with steam. After filtering, the residue in the flask is made permanently mineral acid by means of hydrochloric acid, when the benzoic acid formed comes out in a pure white form on cooling. The steam distillate contains certain other products besides benzaldehyde which cannot be completely removed by fractional distillation. It is therefore dissolved in bisulphite containing 25 % SO_2 and separated, after standing, from the oily portion. 250–350 Gms. sodium bisulphite are required according to the amount of water present. The clear liquid is treated with

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[1] Sunlight or "Uviol-light" facilitates the smooth chlorination in the side chain to a remarkable degree, particularly in the case of the chlortoluenes (*cf.* p. 90 *et seq.*).

soda or caustic soda solution until distinctly alkaline, after which it is separated in a separating funnel and distilled finally under ordinary pressure. *The yield of benzoic acid is about* 12 *gms., that of benzaldehyde up to* 80 *gms.* (*b.p.* 178–179°).

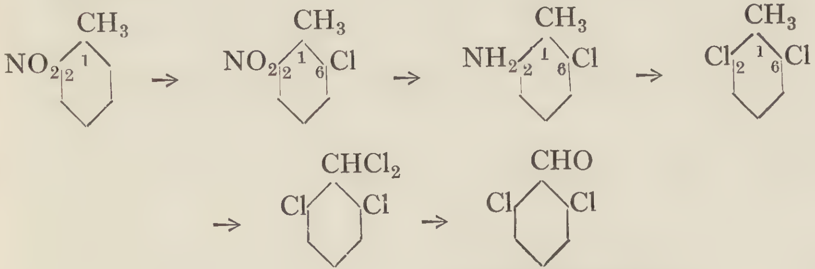
Notes on Works Technique and Practice.—In contrast to benzene, toluene cannot be chlorinated in iron vessels as, in the presence of iron, chlorine enters the benzene nucleus. One is therefore forced to use enamelled or glass vessels for such chlorinations (*cf.* dichlorbenzaldehyde, p. 92 *et seq.*). The addition of phosphorus pentachloride is frequently omitted as it has only an accelerating action, and is not therefore essential. The decomposition of the benzalchloride is effected in copper apparatus and the separation of the benzaldehyde is done in large lead-lined separating funnels provided with observation windows. The method described above (D. R. P. 85493) has completely displaced the older process starting from benzylchloride, which was converted into benzaldehyde by means of water and lead nitrate.

There is, however, another process which is carried out on a large scale, and which favours the formation of benzoic acid, the more expensive product. It consists in oxidizing toluene in concentrated sulphuric acid with pyrolusite or manganite (see Xylene Blue VS.).

Benzaldehyde is not only an intermediate for various dyes, but is used to an even greater extent for scenting the so-called " Milk of Almonds " soap (" Mandelmilch Seife "). The cheaper varieties of this soap are, however, adulterated with nitrobenzene (" Oil of Mirbane "), which may be recognized by the fact that the soap becomes yellow in time.

2:6-Dichlorbenzaldehyde from Orthonitrotoluene.

Reaction :



2:6-*Dichlorbenzaldehyde.*

(a) *Chlornitrotoluene from Orthonitrotoluene.*

Iron is the best catalyst for facilitating the introduction of chlorine into orthonitrotoluene, in particular the so-called steel shavings used for household purposes. The action of iron filings and grey cast-iron borings is too energetic, so that besides 2:6-chlornitrotoluene a considerable quantity of 2:5-dichlortoluene is formed (up to 50 %), which does not yield a good colour.

137 gms. *o*-Nitrotoluene.
76 gms. (38 gms.) Cl_2.
20 gms. Fe.

Into a half-litre bolthead is introduced 1 gm.-molecule (= 137 gms.) of carefully dried orthonitrotoluene together with 20 gms. steel turnings in small pieces, and dry chlorine is passed in with vigorous stirring until the increase in weight amounts to exactly 38 gms. The temperature rises to 40°, the chlorine absorption occupying about three hours. The product is allowed to stand, filtered from iron sludge, and the crude product distilled in vacuo. At 11 mms. pressure the following fractions are obtained :—

100–107°	about 3 gms.
107–114°	about 152 gms.

The resinous product left behind weighs about 8 gms.

If it is desired to purify the product it may be submitted to a further vacuum distillation with a glass-bead column. The chlornitrotoluene so obtained still contains about 10 % of 2:5- and 2:5:6-derivatives which cannot be readily removed. *The yield is about* 94 %. By taking a 10 % excess of chlorine, the 2:5-dichlortoluene is converted for the most part into the 2:5:6-trichlortoluene, which has practically the same properties as the 2:6 product.[1]

(b) 2:6-*Chlortoluidine.*

100 gms. Nitrochlortoluene.
100 gms. Fe.
200 c.cs. H_2O.
20 gms. HCl (30 %).
20 gms. Na_2CO_3.

The reduction of nitrochlortoluene is done by Béchamp's method. 100 Gms. of the nitro compound are added during 2 hours to 100 gms. finely divided iron, 20 gms. crude hydrochloric acid, and 200 c.cs. water at the boil with continuous stirring. The apparatus is then placed in an oil bath, 20 gms. of soda are added and the chlortoluidine distilled off with steam at 140° through an inclined condenser, the temperature of the bath being 200°. It is quite easy to drive all the base over with three parts of water at most. The product is

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[1] The assumption by Jansen (*Chem. Zeutr.* 1110, 1900), that the 2:6-dichlortoluene exists in two modifications is incorrect. The supposed isomer is merely 2:5-nitrochlortoluene.

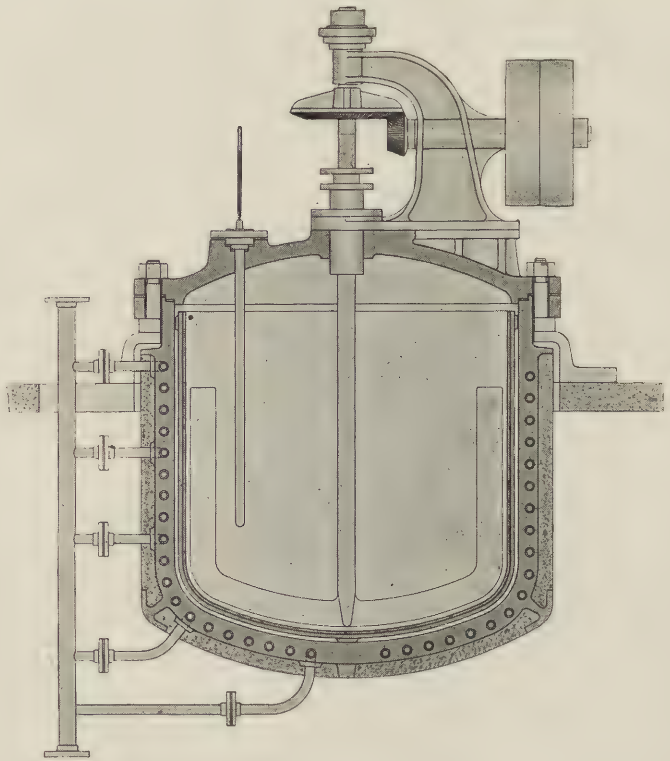

FIG. 23.

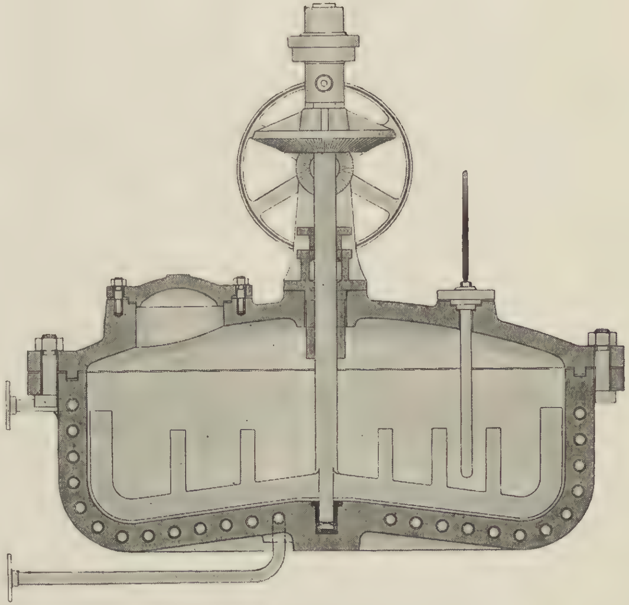

FIG. 24.

Autoclaves fitted for steam or hot-water heating (Frederking system).

then removed with a separating funnel. Purification is effected by vacuum distillation, the boiling point at 10 mms. being 105–110°, or 240° at the ordinary pressure. The distillation is not absolutely necessary but is advisable in order to remove all the iron. *The yield is about* 94 % *of theory.*

(c) 2:6-*Dichlortoluene.*

1 Gm.-molecule (=160 gms.) of chlortoluidine is dissolved at 80° in 1 litre of water and 450 gms. 30 % hydrochloric acid, and the solution is allowed to cool to 30° with stirring. Sufficient ice is then added to reduce the temperature to 5° (a portion of the hydrochloride coming out of solution), and the whole is then diazotized with 70 gms. of 100 % sodium nitrite, dissolved in 200 c.cs. of water (see general instructions). The temperature may be allowed to rise to 16°, the volume occupying about 1·4 litres. As soon as the reaction with nitrite paper persists after 10 minutes, the diazotization may be regarded as complete. The diazonium solution is now allowed to run into a cuprous chloride solution during half an hour, the requisite solution being made from 200 gms. copper sulphate and 200 gms. common salt dissolved in 800 c.cs. water by passing in sulphur dioxide; the excess of SO_2 must first be removed from the solution by boiling.[1]

160 gms. Chlortoluidine.
450 gms. 30 % HCl.
1 litre H_2O.
70 gms. $NaNO_2$.
200 c.cs. H_2O.

200 gms. $CuSO_4 . 5H_2O$.
200 gms. $NaCl + SO_2$.

The copper solution is best boiled up in an earthenware pot by passing in steam, the diazonium solution being added with mechanical stirring. To prevent loss of dichlortoluene the vessel must be well covered in and the temperature must not exceed 95°. The resultant solution is then placed in a 4-litre flask and the dichlortoluene driven over with steam. Approximately 160 gms. are obtained, *i.e.* 88 % of theory, but the resultant product is not sufficiently pure. It is therefore first shaken in a separating funnel with 5 % sulphuric acid (66° Bé.) after which it is washed with water, then purified twice with 40 % caustic soda lye, and finally it is distilled. It comes over at 185–192°; at 192–199° a further fraction of isomers is obtained, most of which can be worked up further with the main fraction. *The yield of absolutely pure dichlortoluene is about* 70 %, *calculated upon nitrotoluene.*

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[1] The cuprous chloride solution may also be prepared in the following manner: 100 gms. copper sulphate are dissolved in half a litre of water, the copper is completely precipitated by the addition of 50 gms. zinc dust, and the supernatant liquid is then poured off. The finely divided copper is warmed with dilute hydrochloric acid until all the zinc is dissolved, after which 100 gms. common salt and a further solution of 100 gms. copper sulphate are added, and the whole warmed to 80° for quarter of an hour.

(d) 2:6-*Dichlorbenzal chloride*.

160 gms. Dichlortoluene.

142 (71) gms. Chlorine.

The chlorination of dichlortoluene to dichlorbenzal chloride is a very simple matter in the laboratory. Chlorine is passed into the dry boiling dichlortoluene, if possible in sunlight, until the increase in weight is 71 gms. for 160 gms. of dichlortoluene. With this quantity the chlorination is easily completed in 2 hours. The vessel must be provided with a very efficient reflux condenser to prevent the hydrochloric acid evolved from carrying off any benzal chloride. As the dichlortoluene used is generally not pure, the product is distilled in vacuo. At 16 mms. about 1 % *dichlorbenzal chloride* comes over at 116–119°, and 95 % *at* 120–130° ; the residue consists of resins and higher chlorinated products. At the ordinary pressure 2:6-dichlorbenzal chloride boils at 250°.

(e) *Hydrolysis of* 2:6-*Dichlorbenzal Chloride*.

This is more difficult than with ordinary benzal chloride ; in contrast to this latter substance it cannot be hydrolysed with water and iron, or with lime or caustic potash, even under pressure at 150°. It is possible, however, to obtain the desired aldehyde by means of concentrated sulphuric acid, although a considerable portion becomes resinified whilst so doing.

100 gms. Dichlorbenzal chloride.

200 gms. H_2SO_4, 66° Bé.

100 Gms. 2:6-dichlorbenzal chloride are stirred with 200 gms. 66° Bé. sulphuric acid at 55° for 12 hours. The solution is then poured into a litre of water, the product run off from the dilute sulphuric acid, and distilled in steam. *Yield about* 30 *gms. pure* 2:6-*dichlorbenzaldehyde. M.p.* 71°.

Notes on Works Technique and Practice.—2:6-Dichlorbenzaldehyde has become a fairly important intermediate in recent years, as it is the starting-point for several colours of the Aurine series (Erio Chrome Azurol, etc.). It is also very interesting from the technical point of view, as it is produced as a result of three types of chlorination. The first two chlorinations offer no difficulty on the large scale, but the third is by no means easy to carry out. The chief difficulty is the unreliability of large glass vessels ; iron, copper, tin, etc., cannot be used, and enamel cracks at such high temperatures. One is therefore forced to carry out the chlorination in a number of small glass carboys, holding 10–15 litres, which are heated on sand-baths by means of gas or on the Frederking system. Owing to the frequent breaking of the glass vessels, steam heating offers the best protection against fire, but at the same time there are such high pressures (200 atm.) in the steam pipes that there is always the possibility of explosions. For this reason the simple sand-bath is usually preferred. Recently attempts have been made to facilitate the introduction of chlorine into the side chain by the use of ultraviolet rays from a Uviol lamp. This only succeeds, however, when there is no trace of iron present in the reaction mixture. Even the minute traces of iron in the quartz lamp, or in the porcelain vessels, or the dust of the factory containing iron rust, may cause serious disturbances. The temperature should be low at first, then rising gradually to 100°.

The preparation of 2:6-dichlortoluene is one of the few technical examples of the application of Sandmeyer's reaction ; so far as I am aware, the only other substance made by this method is 2-chlorbenzaldehyde. The chlorine atom in such compounds may be easily replaced by a sulphonic group on heating to 150° with neutral sulphite. Orthosulphonated benzaldehydes give alkali-fast triphenylmethane colours such as Patent Blue, Erio Glaucine, and Xylene Blue.

In the works the distillation at the various intermediate stages is not performed ; but the dichlortoluene must be distilled to obtain it absolutely dry.

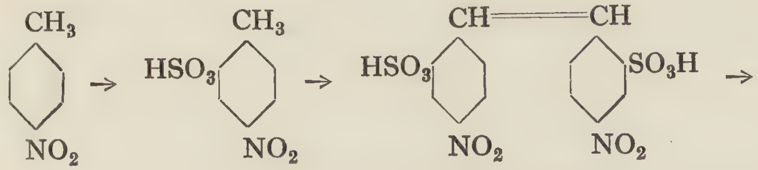
It is sufficient to separate the remaining compounds from their mother-liquors in homogeneously lead-lined separating funnels. The copper solutions are always worked up again for cuprous chloride by means of zinc dust, the loss on a single operation rarely exceeding 2 %.

4. *OXIDATIONS*[1]

Dinitrostilbene-Disulphonic Acid and Diaminostilbene-Disulphonic Acid from *p*-Nitrotoluene.

(Conjoint oxidation of two molecules.)

Reaction :



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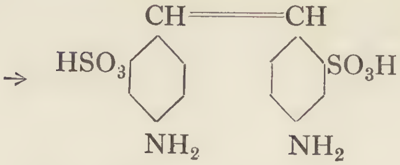
[1] *Cf.* also Malachite Green and Xylene Blue VS.



(a) *Dinitrostilbene-Disulphonic Acid.*

100 gms. *p*-Nitrotoluene.
280–320 gms. 25 % Oleum.
300 gms. H_2O.
300 gms. Ice.
250 gms. NaCl.
50 gms. Soda.
2 l. Water.
160 gms. 35 % NaOH.
1700 gms. 5 % NaOCl (=85 gms. 100 % NaOCl).
300 gms. NaOH (35 %).

oo Gms. *p*-nitrotoluene are sulphonated exactly as described for nitrobenzene, and the product separated as the sodium salt. The press-cakes are dissolved in 500 c.cs. of water at 60° with the aid of soda, about 50 gms. being required ; if more be needed, the cakes were insufficiently pressed. The solution is filtered from iron oxide which is nearly always present, and made up to 2 litres at 50°. To the well-stirred liquid 160 gms. of 35 % caustic soda lye are added during half an hour ; no sodium salt of the sulphonic acid should separate out. A mixture of 1700 gms. sodium hypochlorite solution containing about 5 % NaOCl, and 300 gms. of 35 % caustic soda lye is then allowed to drop in similarly during 10 hours. The strength of the hypochlorite must be exactly determined by titration. It should be remembered that only hypochlorite solutions containing at least 5 % excess NaOH will keep, which is of special importance as regards the preparation of the hypochlorite solution. The temperature must not exceed 56°, as otherwise yellow dyes of the Mikado series are formed.

400 gms. NaCl.

The mixture is now allowed to stand at 55° for at least 24 hours, taking care that free chlorine (hypochlorite) can be detected during the whole period with the aid of potassium iodide-starch paper. It is then cooled to 15°, 400 gms. of salt are added, and the whole is allowed to stand for a day. The sodium salt of dinitrostilbene-disulphonic acid separates out as a yellow crystalline precipitate which is filtered and washed with a very little brine. *The yield of crude salt is about* 100 *gms.*

(b) *Reduction to Diaminostilbene-Disulphonic Acid.*

About 300 c.cs. water.
A little HCl.
200 gms. Fe.
20 c.cs. 40 % Acetic acid.

The sparingly soluble sodium salt is dissolved in 300 c.cs. hot water, the free soda being neutralized with a little dilute hydrochloric acid. This solution is allowed to run on to 200 gms. of iron turnings (which have been etched by means of 20 c.cs. of 40 % acetic acid), during half an hour. The reduction proceeds according to the known method (see, for example, p. 67).

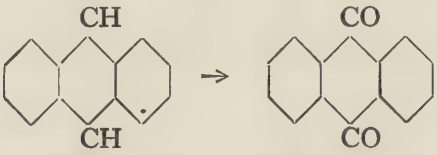
The clear solution is made strongly acid to Congo with hydrochloric acid, whereupon the diaminostilbene-disulphonic acid is precipitated in small yellowish-white crystals. It is filtered off after standing for 10 hours and thoroughly washed. *The yield of sulphonic acid for each* 100 *gms.* p-*nitrotoluene is about* 75 *gms. of* 100 % *product.* In distinction from the analogously constituted 2:2′-benzidine disulphonic acid, it cannot easily be diazotized by the indirect method.

About 15 gms. Na_2CO_3. About 100 gms. 30 % HCl.

Notes on Works Technique and Practice.—The method for the preparation of diaminostilbene-disulphonic acid described here was first given by Green, and, with the lowering of the price of chlorine, it has completely displaced Leonhardt's method. The old process consisted in reducing Mikado Yellow, which was obtained by the action of concentrated soda lye upon *p*-nitrotoluene sulphonic acid. By this method, however, only 48 % of the theoretical yield of diamino acid is obtained even under the most favourable conditions, and large quantities of zinc dust or ammonium sulphide are required for the reduction. Further, all the caustic soda is lost, whilst by Green's process caustic lye, chlorate and common salt can be recovered. Again Green's product is much purer; if too concentrated solutions have not been used it contains absolutely no diamino-dibenzyl disulphonic acid, which weakens Chrysophenin considerably. The presence of the dibenzyl derivative can be readily detected by means of two reactions: first, the dye from H-acid and the dibenzyl acid is much redder than that from the stilbene derivative, and secondly, the "Chrysophenin" from the dibenzyl derivative turns almost reddish-violet with mineral acids, and not a pure blue. A comparatively small content of diamino-dibenzyl disulphonic acid can be recognized at once by comparison with a specimen of the pure colour. The oxidation to the dinitro acid is carried out in concrete vats. It is to be noted that a very small content of iron or even of copper immediately decomposes the hypochlorite solution, wood being inadmissible also for the same reason.

Anthraquinone from Anthracene.

Reaction:



Anthracene. *Anthraquinone.*

The anthracene used for the preparation of anthraquinone should not be too impure, or too much chromic acid will be used up. At the present day, the tar distilleries deliver a product of 80–92 % purity, which is estimated by the recognized methods (*cf.* Lunge, " Untersuchungsmethoden "). The commercial product is crystallized from pyridine.

Before oxidizing, the anthracene must always be sublimed by means of superheated steam at about 200°, as only in this way can it be reduced to a sufficiently fine state of division for use.

300 gms. 100 % Anthracene.
600 gms. $Na_2Cr_2O_7$.
6 l. H_2O.
1800 gms. 50% H_2SO_4.

300 Gms. moist sublimed anthracene, calculated as 100 % product, are stirred up with 6 litres of water in a large lead-lined iron vessel and 600 gms. sodium bichromate are dissolved in it at the same time. The mixture is heated to 80° by means of a Fletcher burner, and 1800 gms. 50 % sulphuric acid are run in from a dropping funnel during 10 hours. The presence of chromic acid must always be clearly shown, and the mixture must be stirred by means of a glass or wooden stirrer ; finally, the mixture is boiled up for 2 hours, replacing the evaporated water. The product is filtered off and thoroughly washed. The mother-liquor may be worked up for chrome alum or for chromic sulphate.[1]

The thoroughly dried crude anthraquinone still contains some unchanged anthracene together with other impurities, and is carefully purified before working up further. Most of the impurities are removed by partial sulphonation, the pure product being finally redistilled with superheated steam.

The powdered and dried crude anthraquinone is heated with two and a half times its weight of 60° Bé. sulphuric acid to 120°, so long as sulphurous acid is evolved. After about 3 hours the mixture is poured into about three times its weight of water, filtered and thoroughly washed. The purified anthraquinone is then sublimed with steam at 240–260°. It is obtained as a fine faintly yellow powder (for apparatus see Fig. 17). *The yield of dried product obtained from* 100 *gms. pure anthracene is about* 106 *parts of sublimed* 100 % *anthraquinone.*

Notes on Works Technique and Practice.—The oxidation of anthracene is carried out in the works in lead-lined wooden vessels, or homogeneously lead-lined iron vessels, of very large dimensions. Vats holding from 15–25 thousand litres are by no means rare. The chromic sulphate which is formed as a by-product plays an important part in calculating the cost of the product, as it finds use for the chrome-tanning of leather.

---

[1] Careful note should be made of the fact that commercial sodium bichromate nearly always has its CrO_3 content reduced to that of the potassium salt by means of Glauber salt.

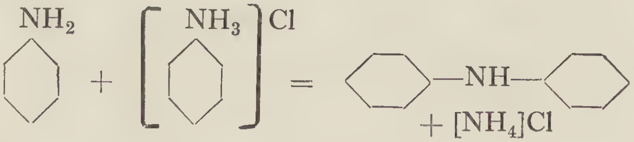
Attempts to obtain anthraquinone by other means, such as nitrous oxides and air, have failed, not on account of any special technical difficulties, but owing to purely business considerations. The B.A.S.F., for instance, attempted the oxidation of anthracene with N_2O_3 in the form of vapour, but had to go back to the old process after a short time, as their leather customers had to be provided with chromic sulphate without fail, and it was not possible to obtain it so cheaply by any other method. The Fabrik Griesheim Elektron are said to carry out the new method with success. This process might also, under some conditions, be of importance, as it is independent of the use of foreign chrome-iron ore. Should the chrome leather tanning be displaced by the newer synthetic tanning materials, then it is quite certain that the chromic acid method would in time gradually disappear.

The distillation of anthracene and anthraquinone is carried out in apparatus very similar to that required for diphenylamine (*cf.* p. 99). The vapours, however, are condensed in large chambers, about 3×3×5 metres, by spraying in cold water. The bottom of the chamber is covered with fine calico, which allows the water to run off, but retains the sublimate.

5. *CONDENSATIONS*

Diphenylamine from Aniline and Aniline Salt.

Reaction :



93 gms. Aniline.

93 gms. Aniline salt.

93 Gms. aniline and 93 gms. aniline hydrochloride (aniline salt) are heated for 20 hours to 230° in an enamelled autoclave fitted with an enamelled thermometer tube. The pressure reaches about 6 atms. If no enamelled thermometer tube is obtainable, it suffices simply to heat up to the requisite pressure and to note the external temperature of the oil bath, which is about 25° higher than the actual internal temperature. After 2 hours, the water present is cautiously blown off through the valve, as even traces have a very unfavourable

70 c.cs.
30 % HCl.

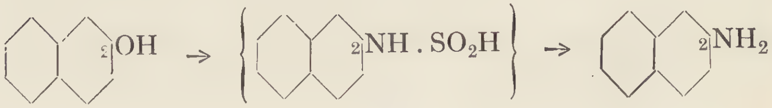
influence on the reaction. This process is repeated three times during the course of an hour, a certain amount of aniline and ammonia also escaping. There is no point in heating for longer than 20 hours, as the only effect would be to diminish the yield. After cooling, the contents of the autoclave are placed in a porcelain dish and treated with a litre of water. The whole is then heated up to 80° and 70 c.cs. of 30 % hydrochloric acid are added until just acid to Congo; it is then allowed to cool down over-night. The crude diphenylamine separates out as a solid cake which can be easily separated from the mother-liquor, as diphenylamine does not form a salt with the dilute hydrochloric acid. After filtering off, it is again melted up with a little water, extracted with a small quantity of hydrochloric acid and washed with dilute sodium carbonate solution.

The diphenylamine so obtained is extremely impure. It must therefore be distilled with superheated steam. For this purpose, it is placed in a half-litre distilling vessel, and the apparatus put together as shown in Fig. 17. The oil-bath is heated to 250°, and the superheater is then started up with an ordinary Fletcher burner. The water must be carefully removed from the steam, the temperature of the superheated steam being about 300°. With a good distillation it is easily possible to get over half-part base for each part water. The diphenylamine is obtained as an almost colourless liquid which solidifies to pale yellow cakes. By pouring into water it is obtained completely pure in a *yield of about* 100 *gms.; m.p.* 51°. About 55 gms. aniline can be recovered from the acid mother-liquors.

Notes on Works Technique and Practice.—The autoclaves employed must be enamelled inside the cover as well as inside the vessel itself. Traces of iron or copper diminish the yield of diphenylamine by 30–50 %, resinous products being formed. The extraction with hydrochloric acid is effected in wooden vats, and the distillation by means of superheated steam is shown in Fig. 19. For superheating, modern appliances are used such as the excellent "Heitzmann Superheater," etc. It is possible to get over one part of diphenylamine with one part of water at 230°.

β-Naphthylamine from β-Naphthol.

Reaction:



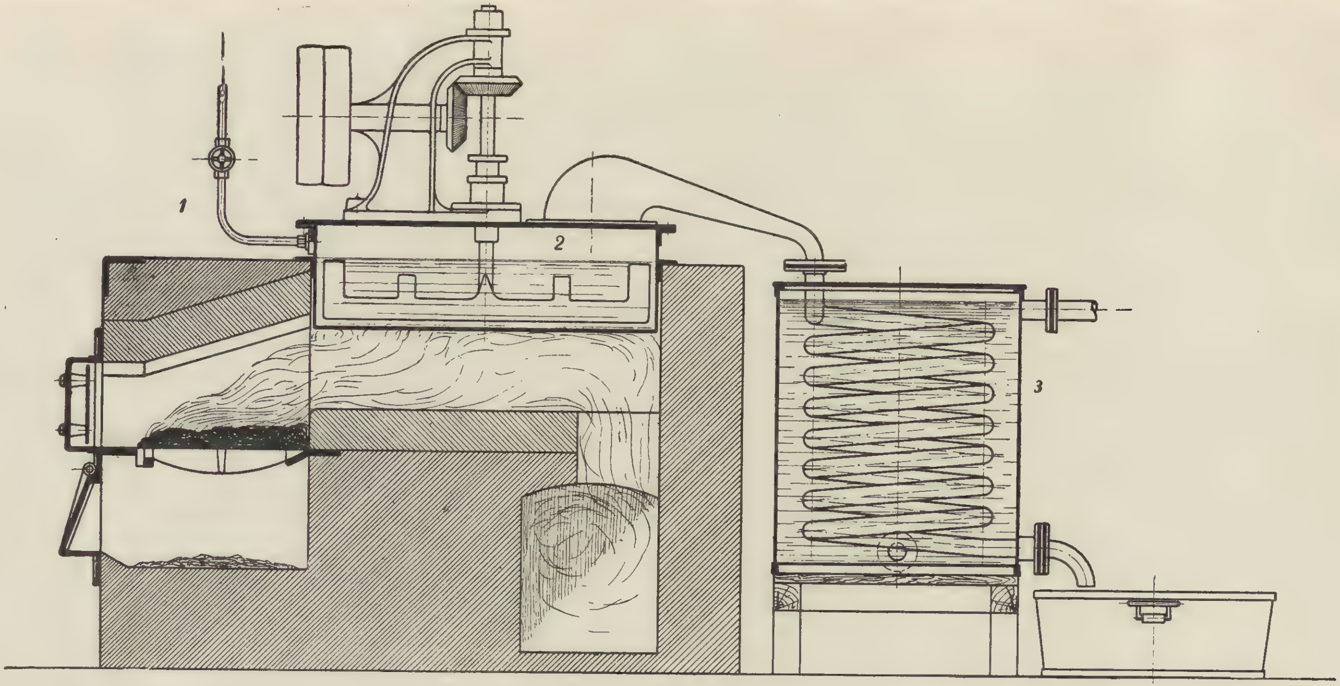


Fig. 19.—Large-scale apparatus for distillation by means of superheated steam, *e.g.* for α-naphthylamine, diphenylamine, etc. (scale, 1:30).

1. Inlet pipe for superheated steam. 2. Still with slowly moving stirrer. 3. Condenser with worm.

On heating naphthol with ammonium sulphite the sulphurous ester of naphthylamine is formed. The excess of ammonia then immediately converts it into naphthylamine and ammonium sulphite.

144 gms.
β-Naphthol.
600 gms.
$(NH_4)_2SO_3$
(22 %).
125 gms.
20 % NH_3.

110 gms.
30 % HCl.
1½ litres H_2O.

200 gms.
Na_2SO_4.

144 Gms. (1 mol.) 100 % β-naphthol and 600 gms. ammonium sulphite are heated up in an autoclave provided with a stirrer and oil-bath.[1] In addition 125 gms. of 20 % ammonia are also added. The mixture is heated for 8 hours at an internal temperature of 150°, and a pressure of about 6 atms. (N.B. steel-tube manometer). The contents are then allowed to cool, and the resultant cake of β-naphthylamine is broken up in a mortar, after which the mass is thoroughly washed out with water from a suction filter. The ammonium sulphite solution may be used several times. The well-washed base is dissolved in 1½ litres of water and 110 gms. hydrochloric acid—which must contain no sulphuric acid—and filtered warm, a certain amount of naphthol remaining behind. The filtrate is treated with a solution of 200 gms. calcined Glauber salt dissolved in 200 c.cs. of water, the naphthylamine being precipitated as naphthylamine sulphate. It is then allowed to stand all night, the precipitate being then filtered off and well washed with cold water. For many purposes the dried sulphate is used directly (*cf.* p. 37).

To obtain the free base the moist sulphate is stirred up with a litre of water and treated with 60 gms. calcined soda dissolved in a little water. Owing to the sparing solubility of the sulphate, the decomposition takes several hours, but may be speeded up by continuous stirring and heating to 80^{c}. The product is then filtered off, washed and dried at 80°.

Yield about 130 *gms. dry base, or* 85–95 % *of theory.*

Notes on Works Technique and Practice.—For reactions of this type it is absolutely essential to use autoclaves fitted with an oil-bath or steam-jacket. The naphthylamine separates out as an oily layer at the bottom of the reaction vessel so that, in spite of stirring, if no oil-bath be used, overheating is bound to occur, leading to the conversion of a considerable portion into dinaphthylamine and decomposition products. This also holds good for the preparation of α-naphthol (see p. 102).

For technical purposes, the β-naphthylamine is usually distilled in vacuo, but great care must be taken, as it easily decomposes. If the base is not isolated, the well-dried, finely powdered sulphate mixed with 1 % of soda (*cf.* also Primuline) is added to the sulphuric acid or oleum as the case may be.

---

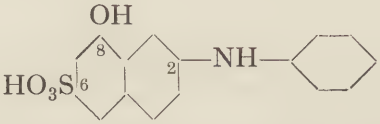
[1] Ammonium sulphite is obtained by saturating 250 gms. of 20 % ammonia with SO_2 and then mixing the ammonium bisulphite so obtained with 250 gms. ammonia.

Bucherer's method has completely displaced the older way of heating naphthol with ammonia as this gives only 70 % yields, and requires pressure of 50–60 atms.

The Bucherer reaction may also be used for other substances, and is reversible. For example, by heating H-acid or γ-acid with aniline, sodium bisulphite, and water under a reflux condenser, the corresponding phenylated amino-naphthol sulphonic acids are easily obtained, *e.g.*

(a) *Phenyl-γ-acid.*

Formula :

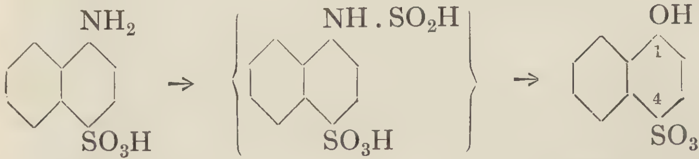


224 Gms. 100 % γ-acid, 750 gms. sodium bisulphite (25 % SO_2), 750 c.cs. water and 200 gms. aniline are heated under a reflux for 24 hours. Sufficient concentrated sodium carbonate solution is then added to give a distinctly alkaline reaction, and the aniline is distilled off with steam. On acidifying with hydrochloric acid the pure phenyl-γ-acid is precipitated. *Yield about* 90 % = 270 *gms.* 90 % *acid.*

224 gms. γ-acid.
750 gms. 25 % $NaHSO_3$.
750 c.cs. H_2O.
200 gms. Aniline.

(b) *Nevile and Winther's acid.*

Reaction :



Naphthionic acid.

Naphthol sulphonic acid 1:4.
Nevile and Winther.

100 Gms. of 100 % naphthionate, dissolved in 200 c.cs. of water, are boiled for a day under a reflux with 600 gms. of sodium bisulphite solution (25 % SO_2). Sufficient 30 % caustic soda solution is then added to redden thiazole paper, and the whole is boiled so long as ammonia is evolved. The product is then made permanently mineral-acid with hydrochloric acid, the crystalline Nevile-Winther acid being obtained on cooling ; it is separated from the residual naphthionic acid by redissolving and filtering. *Yield up to* 80 % *of theory.*

100 gms. 100 % Naphthionic acid.
200 c.cs. H_2O.
600 gms. 25 % $NaHSO_3$

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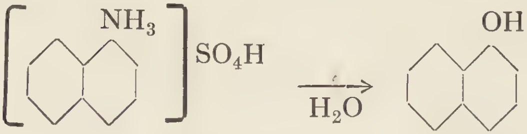
α-Naphthol from α-Naphthylamine.

Reaction :



α-Naphthol.

143 gms.
α-Naphthylamine.
110 gms.
H_2SO_4,
66° Bé.
1 litre H_2O.

143 Gms. α-naphthylamine are mixed with 110 gms. 66 % Bé. sulphuric acid and 1 litre of water, and the whole heated to 200° at 14 atms. pressure. The naphthylamine should first be melted in the hot water and the acid then added in a thin stream with good stirring. The autoclave should be either lead-lined or enamelled and provided with a good stirrer ; the cover may be made of iron, as the sulphuric acid is not volatile. Here also it is necessary that the autoclave should be oil-heated in order to prevent any overheating, otherwise, especially in the works, the lead will certainly be melted.

After 8 hours it is cooled down and the naphthol separated from the mother-liquor, the ammonium sulphate being recovered from the latter. The α-naphthol is melted with a little water, and after solidifying, separated from the liquid ; it is almost chemically pure. To obtain it absolutely pure, vacuum distillation is resorted to. *Yield*, 94–95 % *of theory*. *M.p.* 94°.

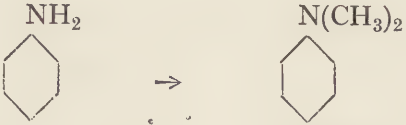
Notes on Works Technique and Practice.—The process described above is the cheapest and best. There is, however, another which is analogous to the preparation of β-naphthol. The sodium salt of α-naphthalene sulphonic acid is melted with caustic soda at 290–300°. The sulphonation is carried out at 80–90°, and the salting out effected in as concentrated a solution as possible. Here also the excess of acid may be removed with advantage by milk of lime or chalk, after which the product is treated with soda, and the evaporated sodium salt melted up without further treatment. The α-naphthol so obtained is impure.

Dimethylaniline.

(Diethyl- and ethylbenzyl-aniline.)

Reaction :

(*a*)



Dimethylaniline.

PLATE IX.

DIPHLEGMATING COLUMNS.

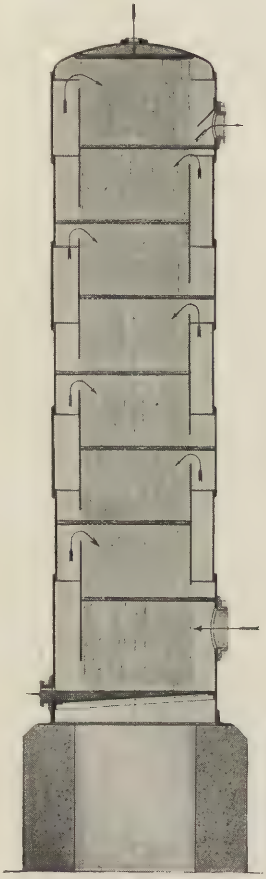


FIG. 25.

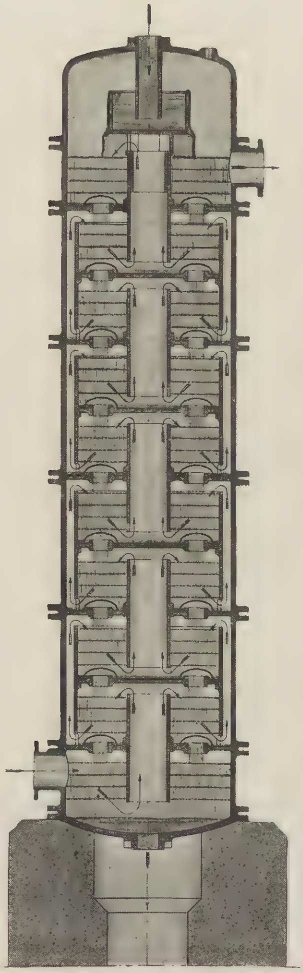


FIG. 25A.

Kubierschky Columns.

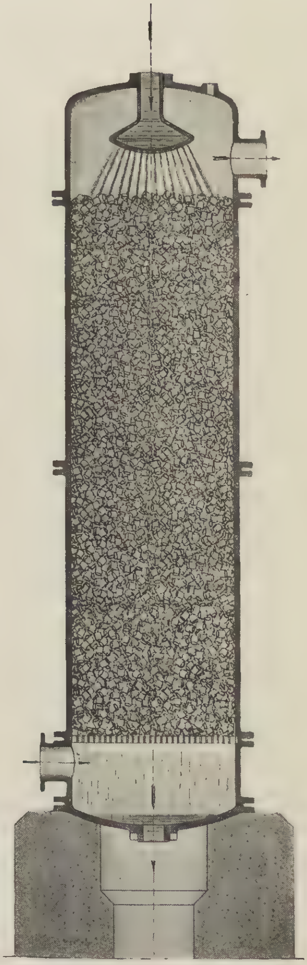
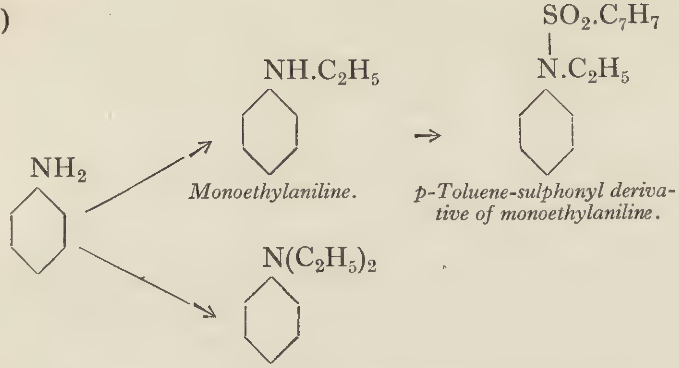


FIG. 26.

Raschig Column.

Diameter of columns, 50–150 cms. Height, 8–16 cms. The upper part (1–2 metres) is externally cooled during rectification. The remainder of the column (7–15 metres) is well insulated, and the top opening is closed.

(*b*)



Monoethylaniline.

p-Toluene-sulphonyl derivative of monoethylaniline.

Diethylaniline.

For the preparation of dimethylaniline an iron autoclave is used with a cast-iron lining, working up to 60 atms. pressure and provided with oil bath, manometer, etc. The methyl alcohol (wood spirit) used for the alkylation must contain no traces of acetone or ethyl alcohol, as the presence of such impurities leads to an immense increase in the pressure; its purity must therefore be tested by means of the iodoform reaction.

93 Gms. of pure aniline are mixed with 105 gms. pure methyl alcohol and 9·4 gms. of 94 % (66° Bé.) sulphuric acid. The autoclave is then closed and the oil-bath heated to 200°; the pressure rises to about 30 atms. and the contents are then left for 6 hours at 215°. They are allowed to cool and are then treated with 25 gms. 30 % caustic soda lye. In order to split up the sulpho-ammonium bases formed at the same time (which are only decomposed at higher temperatures into sulphuric acid, alcohol and tertiary amine), the product must be heated up to 170° in the autoclave for a further 5 hours.[1] The contents of the autoclave are distilled over with steam, the dimethylaniline completely salted out from the aqueous solution with common salt, after which it is removed with a separating funnel and distilled through a small bulb column. It is obtained almost chemically pure as a colourless liquid which contains, however, always some monomethylaniline.[2] *Yield about* 117 *gms*. *B.p.* 192°.

93 gms. Aniline.
105 gms. CH_3OH.
9·4 gms. H_2SO_4, 66° Bé.
25 gms. 30 % NaOH.

(b) *Diethylaniline.*

The preparation of diethylaniline in the laboratory is also quite simple, but should only be carried out in enamelled autoclaves, as hydrochloric acid is used instead of sulphuric acid, ethyl alcohol being simply split up by sulphuric acid into water, carbon, and ethylene.

---

[1] The formation of quaternary ammonium bases is especially noticeable in the preparation of ethylbenzyl-aniline and methylbenzyl-aniline.

[2] The purity may be tested by mixing 4 c.cs. of the dimethylaniline with 2 c.cs. of acetic anhydride. The temperature should not rise more than 1° at most (acetic anhydride test).

130 gms. Aniline salt.
140 gms. Alcohol.

130 Gms. dried aniline hydrochloride are heated with 140 gms. of 95 % alcohol to 180° for 8 hours in an enamelled autoclave. The pressure rises to 30 atms. If a very strong autoclave is available, the contents may be heated with advantage to 200°, pressures up to 55 atms. being produced. After cooling, the contents of the autoclave are placed in a glass bolthead, the alcohol and ethyl ether distilled off, and the residual mixture of mono- and diethylaniline treated with 110 gms. of 30 % caustic soda solution. This product is then stirred up thoroughly at the ordinary temperature with about 40 gms. of para-toluene sulphonic chloride. By this means the monoethylaniline is converted into the toluene sulphonic derivative, which is not volatile in steam, so that the diethylaniline may be distilled over quite pure. The purity is tested by the acetic anhydride test, the sulphonic chloride treatment being repeated if necessary. *Yield about* 120 *gms.*

110 gms. 30 % NaOH.
40 gms. *p*-Toluene sulphonic chloride.

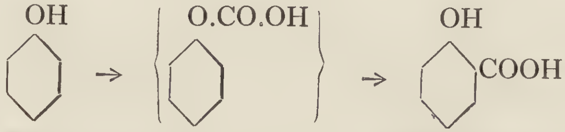
The residual toluene sulphonic derivative may be hydrolysed with concentrated sulphuric acid, and the monoethylaniline recovered.

Notes on Works Technique and Practice.—The heating up of a big autoclave in the works takes from 4–6 hours, and must be carried out very cautiously. As soon as the temperature has reached about 190° the pressure rises rapidly by itself to 10–30 atms. After the reaction is finished, the excess of methyl alcohol is blown off, together with the ether, the vapours being condensed. The hydrolysis of the sulpho-ammonium base is carried out in huge boilers containing from 3000–5000 kgs. dimethylaniline.

The method given above for the preparation of dimethyl- and diethyl-aniline is not very satisfactory, but may be recommended as a simple process. A cheaper and more rational method of preparation consists in using less alcohol and acid, the resultant mixture being saponified directly with caustic soda lye. The monoalkyl derivative is then converted into the alkyl benzyl derivative by means of benzyl chloride ; this process is effected according to the scheme given for the preparation of Chrysophenin and nitrophenetole, or simply by heating the monoalkyl derivative in a closed vessel at 125° with the necessary quantities of benzyl chloride and 50 % caustic soda lye ; 105 % of theory of benzyl chloride is needed. In this manner it is possible to arrange to obtain any required quantity of dialkyl aniline or of mixed amine. The separation is effected by means of steam distillation, the non-volatile benzyl derivative remaining behind. Complete purification is effected by fractional distillation in vacuo; only absolutely pure products give the best yields of dyes of the Acid Violet or Patent Blue series.

Salicylic Acid from Phenol.

Reaction:



Phenol. *Salicylic acid.*

At the present day salicylic acid is made exclusively by the Kolbe-Schmitt method, which consists in treating sodium phenate with dry carbonic acid at first at the ordinary temperature, and then at 125° under 4–7 atms. pressure. The preparation is practically quantitative if the salt is absolutely dry and very finely divided, which may be attained by drying and grinding the substance in a vacuum.

93 gms. Phenol.

40·1 gms. 100 % NaOH.

93 Gms. of pure phenol are placed in an autoclave provided with a valve for the introduction of carbonic acid (Plates I. and XIII.), together with 1 gm.-molecule (40·1 gms. 100 %) caustic soda, free from carbonate, dissolved in 100 gms. water.[1] The solution is evaporated at 100° with continuous stirring under reduced pressure, until no more water comes off. The dried phenate is then removed from the autoclave and powdered as rapidly as possible in a previously heated porcelain basin. In order to protect it from moisture it is at once reintroduced into the autoclave together with 5–10 balls of about 14 mms. diameter made of iron or stone, which serve to pulverize it further during the stirring; the mass is again heated to 165° in vacuo until absolutely dry, which requires 5–6 hours, after which it is cooled down to 30°, and then carbon dioxide is led into the apparatus from a cylinder, with continuous stirring. By means of the reducing valve on the cylinder, the pressure is regulated so that it does not rise higher than 1 atm. After 2 hours the pressure is slowly increased to 5 atms., and the temperature to 125°; after a further hour the tube is disconnected and the pressure let off. When the product has cooled the powdery yellowish salicylate is dissolved in 400 c.cs. water and precipitated with 125 gms. hydrochloric acid (30 %). The salicylic acid, which comes out in a practically pure

400 c.cs. H_2O.

125 gms. HCl.

---

[1] The caustic soda is completely freed from carbonate by dissolving in its own weight of water and allowing to stand for a day at 50°. The solution, after filtering through asbestos, is titrated, using phenolphthalein as indicator.

5% $SnCl_2$.

form, is filtered at 30°, and the traces of phenol washed away with a little water. For the further purification it may either be distilled with super-heated steam at 140°, or be recrystallized from hot water, after precipitating the impurities by means of 50 % of its weight of stannous chloride.[1]

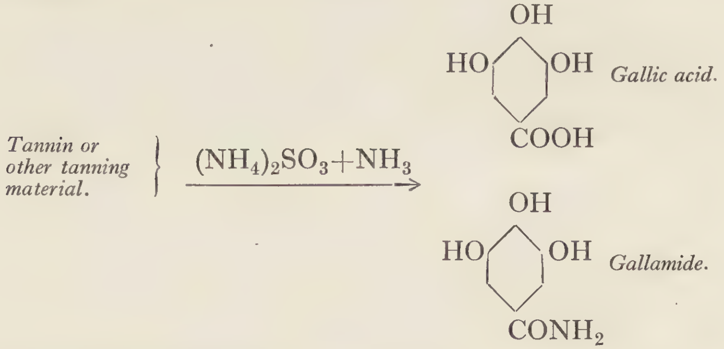
The yield of pure distilled salicylic acid is 125 gms. from 93 gms. phenol.

Notes on Works Technique and Practice.—The equipment used in the works is modelled on the laboratory apparatus, but very powerful stirring-gear and grinding balls are used from the start, so as to make it unnecessary to remove the salt from the autoclave for powdering. Special stirring-gears are also made for this purpose with interlacing arms, which render the balls superfluous. To purify the salicylic acid it may be sublimed in a current of hot air, a beautiful product being obtained in this manner, which is, however, not quite pure. The yield of colours obtained from the distilled acid is always better. The process is almost quantitative, up to 137 kilos salicylic acid being obtained from 93 kilos phenol.

In a similar manner, ortho-cresotinic acid is obtained from ortho-cresol. In this case, however, the operation must be carried right through from start to finish without interruption as the sodium salt of ortho-cresol is spontaneously inflammable. About 20 % of the ortho-cresol is recovered unchanged, and the cresotinic acid must be reprecipitated from water.[2] In spite of this, however, it is no more expensive than salicylic acid, as the poor yields are made up for by the cheapness of the cresol.

Gallamide and Gallic Acid from Tannin.

Reaction :



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[1] D. R. P. 65131 (1892).

[2] It is dissolved in soda, the boiling solution precipitated with hydrochloric acid, and the liquid filtered hot.

The most important raw material for gallamide and gallic acid are Gall-nuts and Sumach (*Rhus coriaria*). The tannin is either hydrolysed by caustic soda into sugar and gallic acid, or by the action of ammonium sulphite into sugar, gallic acid and gallamide, approximately equal parts of amide and acid being obtained.

200 Gms. tannin together with 200 c.cs. water, 400 gms. 20 % ammonia, and 100 gms. sodium bisulphite solution (25 % SO_2) are placed in a soda-water bottle fitted with a rubber stopper, which is then heated for 12 hours in a water bath at 50°. The bottle must be shaken occasionally to ensure complete solution. The solution is then concentrated in a large glass flask to 400 c.cs. under reduced pressure.

200 gms.
Tannin.
200 gms.
H_2O.
400 gms.
20 % NH_3.
100 gms.
25 %
$NaHSO_3$.

After cooling, sufficient hydrochloric acid is added cautiously to render the liquid just acid to litmus. The gallamide is completely precipitated within 24 hours. (In the laboratory it is frequently necessary to cool down a small portion in a freezing mixture, and then to scratch the inside of the vessel in order to start the crystallization.)

The sparingly soluble gallamide is filtered off and well washed. The mother-liquor is treated with 100 gms. of 30 % caustic soda lye and the ammonia removed in vacuo. The liquid is then concentrated again to 300 c.cs. and acidified with sufficient concentrated hydrochloric acid to turn Congo paper just blue. The sodium salt of gallic acid separates out in the course of a few days in the form of a finely crystalline precipitate which is filtered off and pressed without washing. It is dissolved in 100 c.cs. water, and the gallic acid precipitated from the solution by means of hydrochloric acid. *Yield of gallamide and gallic acid about* 60 *gms. each.*

100 gms.
30 % NaOH.

Notes on Works Technique and Practice.—On the large scale, solutions of tannin are used which are obtained by extracting the material containing the tannin with hot soft water on the counter-current principle, the solutions being afterwards evaporated in vacuo to 30° Bé. The process is carried out in large concrete vats which may be used either for positive or negative pressures. The crystallization of the gallamide takes from 10–14 days, and that of the gallate still longer. Tannin solutions ferment readily, so that it is necessary to work quickly, particularly during the summer months. The purity of the gallamide is estimated by distilling off the ammonia from a weighed portion, by means of caustic soda, which is absorbed in normal hydrochloric acid, and the latter titrated back. Good gallamide should be 92 % pure.

Gallamide and gallic acid are used in large quantities for the preparation of Oxazines (see Gallamine Blue).

II. DYES

6. AZO DYES

As the azo colours form at the present day by far the largest group of synthetic organic colouring matters, I have prefaced the sections dealing with these products by certain general methods, as in many cases the diazotization and coupling takes place according to certain well-defined rules. Exact rules, however, cannot be laid down, as each amine and each phenol has its own peculiarities which must first be accurately determined by experiment. As it is not possible to go fully into details in this book, we must content ourselves with a few typical examples. The methods of analysis are given in the analytical portion.

Diazotization of Amines.

Aromatic amines are diazotized, usually at 5–10°, in as concentrated a solution as possible. According to the nature of the amine a greater or less quantity of acid is used, hydrochloric acid being nearly always taken for this purpose, as sulphuric or nitric acids are only of use in exceptional cases. In the works, however, sulphuric acid is frequently used, owing to its cheapness, but it has the disadvantage that, on salting out the finished dye, Glauber salt crystallizes out, which weakens the colour and may even make it unfilterable.

Aniline.

(Toluidine ; Xylidine ; Meta-nitraniline.)

9·3 Gms. (1/10 mol.) aniline are stirred up by means of a glass rod with 30 c.cs. hot water and 25 c.cs. concentrated hydrochloric acid are then added in a thin stream. The solution is allowed to cool somewhat, and when it has reached 40° sufficient ice is added to bring the temperature down to 0°, leaving a slight excess of ice. A solution of 7 gms. 100 % sodium nitrite (20 % solution)[1] is then added rapidly with vigorous stirring. This solution of nitrite is best kept as a stock solution standardized by means of pure sulphanilic acid. The diazotization is complete as soon as a drop of the diazonium solution reacts with potassium iodide paper and with Congo paper. Every diazotization should be followed by means of both of these reagents. The diazotization occupies about 2 minutes (half an hour on the large scale), the end-temperature being about 7° and the total volume about 250 c.cs.

In the cases of *p*-toluidine and chloraniline a certain amount of the hydrochloride often separates out during the ice-cooling, but rapidly disappears during the diazotization.

p-Nitraniline.

(*o*-Nitraniline, etc.)

As the salts of *p*-nitraniline are unstable in aqueous solution, the base must be brought into reaction in a very finely divided condition.

14·5 Gms. (1/10 mol.) commercial nitraniline are dissolved in 30 c.cs. concentrated hydrochloric acid and 30 c.cs. water at 80–90°, and the clear solution is then allowed to flow in a fine stream on to 50 c.cs. of water and 50 gms. of finely crushed ice with good stirring ; final temperature about 80°. 7 Gms. sodium nitrite as 20 % solution are then run in with vigorous stirring ; the temperature rises to 15°, and the solution becomes clear in a few seconds. The liquid is tested with Congo- and nitrite-paper. On the large scale, also, the nitrite must be run in very rapidly *under* the surface of the liquid, as otherwise considerable quantities of diazo-amino compounds are formed.

α-Naphthylamine.

14·3 Gms. (1/10 mol.) α-naphthylamine are dissolved in 22 gms. 30 % hydrochloric acid and 100 c.cs. hot water, and the solution is then cooled down to 0° with 200 gms. ice. 60 Gms. salt are added, and, as soon as the temperature has gone down to –5°, 20 gms. 20 % sulphuric acid, and then, quickly, 7 gms. 100 % sodium nitrite as 20 % solution. The diazotization is completed in a few minutes, the sparingly soluble sulphate of naphthylamine going into solution. The final volume is about 800 c.cs. and the temperature below 0°.

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[1] Volume per cent. : 1 litre=200 gms. 100 % sodium nitrite.

Sulphanilic Acid.

(Metanilic Acid, Naphthionic Acid, Nitraniline Sulphonic Acids, Chloraniline Sulphonic Acids, Diamino-Stilbene Disulphonic Acid, Primuline Sulphonic Acid, etc.)

17·3 Gms. (1/10 mol.) 100 % sulphanilic acid are dissolved in 100 c.cs. of water with the aid of 5·5 gms. soda.[1] 25 C.cs. hydrochloric acid are added and the whole diazotized with 35 c.cs. 20 % sodium nitrite solution with good stirring. The diazotization takes about 10 minutes, and the temperature may be allowed to reach 15°.

Diazo compounds which contain a sulphonic group are usually sparingly soluble and come down as their internal anhydrides in the form of white or yellow crystalline precipitates. As, in addition, many amino sulphonic acids are also sparingly soluble, it is necessary to diazotize them indirectly. For this purpose the sodium salt of the sulphonic acid is mixed with the necessary quantity of the sodium nitrite and the mixture is then poured into the acid.

Further difficulties are caused by the fact that certain amines couple with themselves, for instance, Cleve acid, and for these an excess of about 5 % sodium nitrite is necessary.

Benzidine.

(*o*-Tolidine, *o*-Dianisidine.)

18·6 Gms. (1/10 mol.) of technically pure benzidine are dissolved in 23 c.cs. of 30 % hydrochloric acid and 100 c.cs. water at 70°.[2] The solution is cooled to 30–40° when 50 gms. ice are added, a portion of the hydrochloride being precipitated. A further 23 c.cs. hydrochloric acid, diluted with a little water, are then added with good stirring, a fresh quantity of the salt coming out. 70 C.cs. of 20 % sodium nitrite solution are then run in rapidly within 10 seconds. The temperature is about 10–12°, and the solution should become clear in one minute. If the temperature has been kept too low the last traces of benzidine sulphate may remain until 8 or 10 minutes have elapsed. The solution is tested in the usual way with Congo- and nitrite-papers; it is practically neutral, but no diazo-amino compound is formed in this case as with aniline.

---

[1] Sulphonic acids which are already in the form of their salts are, of course, merely dissolved in water.

[2] To obtain quite clear solutions, it is necessary to use hydrochloric acid free from sulphuric acid.

Tolidine and dianisidine must not be boiled, but are best dissolved below 40°, or the finely divided substance is stirred up to a paste with water. In the works the solutions, together with half the hydrochloric acid, are allowed to stand over-night, the ice and remainder of the hydrochloric acid being added next day.

The Coupling of an Azo Component.

Diazo compounds are distinguished as strong or weak coupling substances according to whether they combine with salicylic acid or not. In many cases the combination may be brought about by the use of a large excess of soda or caustic soda lye, though often even this expedient fails, as many diazo compounds, indeed, are decomposed by alkali before the coupling takes place, and in these cases it is necessary to use sodium acetate or formate to combine with the mineral acid which is set free. Generally speaking it may be said that the diazo solution must be run into the phenol or amine; there are very few exceptions to this rule.

A general scheme for coupling is given here which may, in many cases, be made use of just as it stands.

1/10 gm.-molecule phenol (naphthol, amino-naphthol sulphonic acid, etc.) is dissolved in 15 c.cs. of 30 % caustic soda solution and 25 gms. sodium carbonate, together with the necessary quantity of water, and the whole cooled with ice to 0°. The more concentrated the solution, the more smoothly will the coupling take place; the more acid used for diazotizing, the more alkali will be necessary.[1] The diazonium solution (diazo compound) is allowed to run in a thin stream into this cold solution, the whole being stirred gently for 1 hour at a low temperature. The temperature is then raised to 30° in the course of an hour, the liquid is allowed to stand over-night, and next day the dye is separated out at a suitable temperature.

The conditions necessary for separating out the dye are very varied: it may either be filtered off in the cold directly after coupling, or it may be heated up and taken into solution, and then reprecipitated either by salting out or acidifying. In rare cases it may be impossible to separate out the dye, and one is forced to evaporate down the whole solution to dryness.

In the case of amines the scheme for the coupling needs modification in that the base is dissolved in acid (hydrochloric, acetic, or formic acid), and the alkali is replaced by acetate or formate. In very rare cases no addition is necessary, as the coupling takes place spontaneously with elimination of mineral acid. Certain amines insoluble in water, such as diphenylamine, cresidine, α-naphthylamine, etc., are sometimes coupled in alcoholic solution (*cf.* Tropæolin).

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[1] Very strongly acid diazonium solutions are neutralized with soda before coupling.

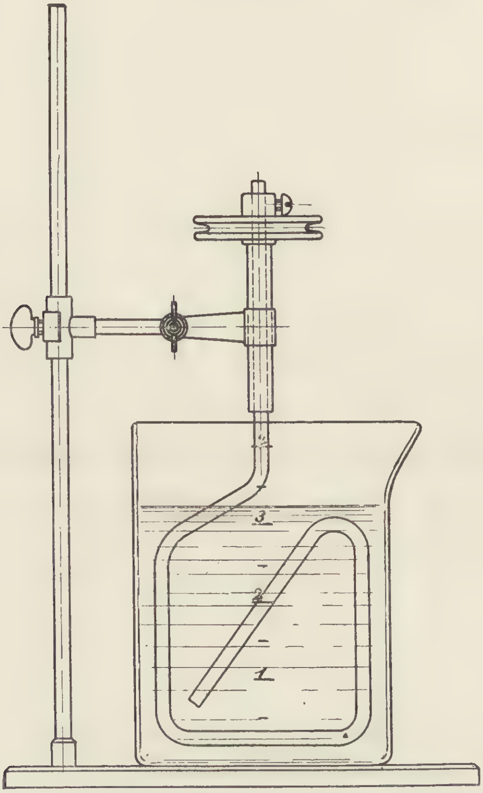


Fig. 21.—Calibrated vessel for coupling.

The pot illustrated above (Fig. 21) is specially suited for coupling. The rough graduation makes it easier to estimate the quantity of fluid present.

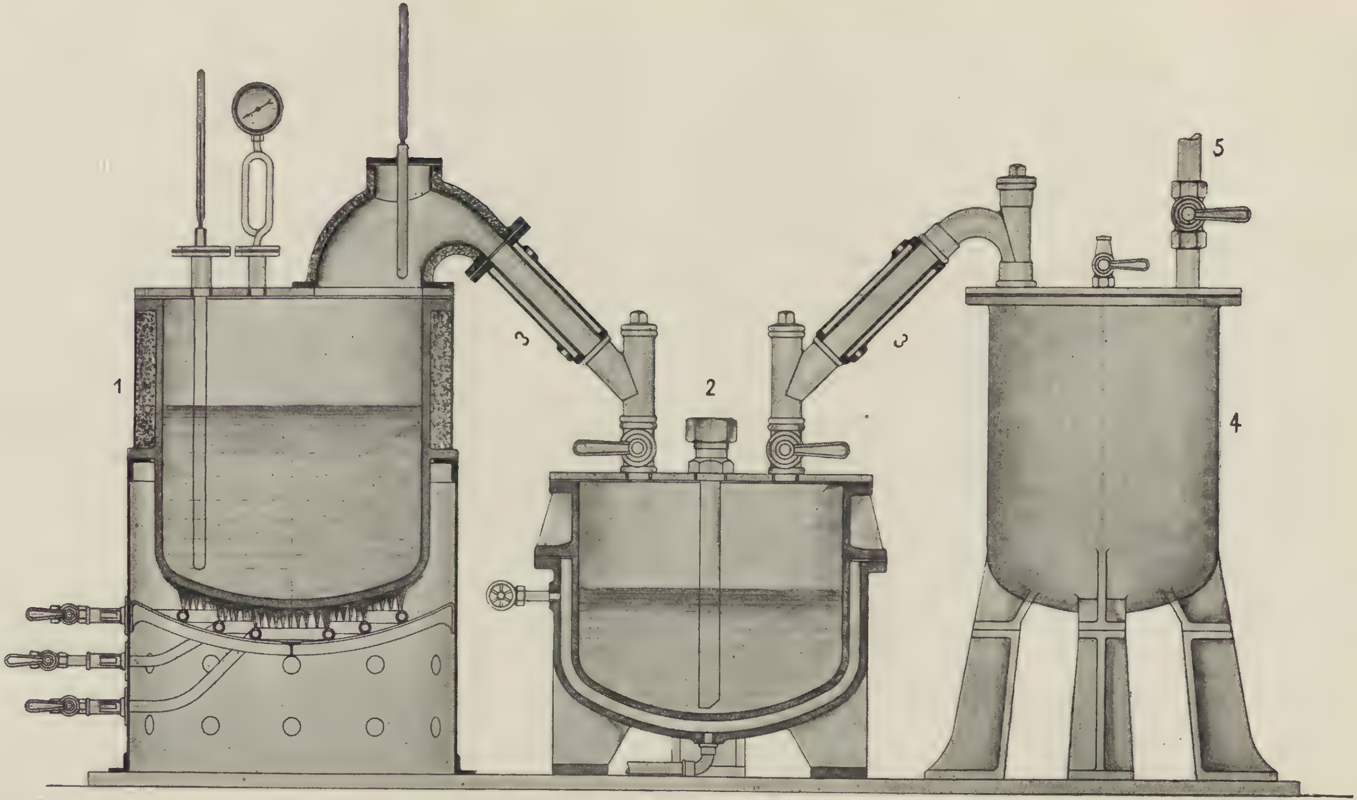
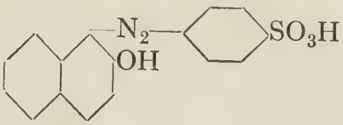


FIG. 28.—Arrangement of plant for vacuum distillation of substances which solidify readily (Naphthols, Phenylenediamine, etc.). 1. Distilling vessel. 2. Receiver with steam- or cooling-jacket. 3. Steam-heated tubes to prevent solidification. 4. Empty vessel for water and sublimate. 5. To pump.

EXAMPLES OF SIMPLE ALKALINE COUPLINGS.

Acid Orange A or Orange II.

Formula :



17·3 Gms. (1/10 mol.) of 100 % sulphanilic acid are dissolved in 200 c.cs. water and 6 gms. soda, any excess of aniline present being driven off with steam by boiling. After filtering, 30 c.cs. concentrated hydrochloric acid are added, and the whole cooled down to 20°. By means of a little ice, the temperature is brought down to 10°, and the liquid is then diazotized below 15° with 7 gms. 100 % sodium nitrite until a permanent reaction is given with nitrite- and Congo-papers.

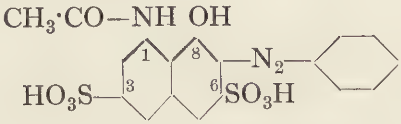
At the same time 14·2 gms. (1/10 mol.) β-naphthol are dissolved in 15 gms. of 30 % caustic soda solution, 25 gms. soda, and 200 c.cs. water ; the β-naphthol should dissolve to a clear solution. The naphthol solution is cooled to 3° with ice, and the suspension of diazo sulphanilic acid added in a thin stream, the temperature being kept below 8°. After the lapse of 1 hour, the dye formed is heated to boiling in a porcelain basin over a bare flame, and the boiling solution is treated with 100 gms. common salt added by degrees. The precipitate, which never goes completely into solution, now separates out completely, and can easily be filtered at 50° on a large suction funnel. The filter-cakes are squeezed in a screw-press, after which they are dried at 100°. *The yield is about* 50 *gms.*, but can only be determined exactly by making comparative dyeing tests.

17·3 gms. Sulphanilic acid.
6 gms. Soda.
200 c.cs. H_2O.
30 c.cs. HCl (30 %).
7 gms. $NaNO_2$ (100 %).
14·2 gms. β-Naphthol.
15 gms. 30 % NaOH.
25 gms. Na_2CO_3.
200 c.cs. H_2O.
Ice.

Notes on Works Technique and Practice.—Owing to its cheapness and brilliant shade, Acid Orange A is one of the most widely used monoazo dyes. In the works the coupling is carried out in very large pitch-pine tubs holding 15,000 and more litres, or in concrete vats lined with pieces of earthenware, holding up to 40 cubic metres. The illustration on Plate VII. shows the general works arrangement with the diazotizing and coupling tubs, together with the pressure vessel (Montejus) and the filter-press. The filtered colour is not pressed hydraulically, but is blown through in the filter-press with compressed air for 1–3 hours, and is then dried directly on copper trays. For this purpose vacuum drying ovens are coming more and more into use, as they not only facilitate rapid drying, but also afford considerable protection to the dye. The calculations for this colouring matter are given in detail later on (*q.v*).

Acetyl-H-Acid and Amidonaphthol Red G.

Formula :



34·1 gms. 100 % H-acid.
5·8 gms. Na_2CO_3.
200 c.cs. H_2O at 70° C.
17 gms. Ac_2O.

34·1 Gms. (1/10 mol.) of 100 % H-acid are dissolved in 200 c.cs. water and 5·8 gms. soda, at 70°. To this is added within about 20 seconds, 17 gms. acetic anhydride with vigorous stirring, by which means the amino group of the H-acid is completely acetylated. The completeness of the acetylation is determined by acidifying a small test portion of the solution with hydrochloric acid, adding a few drops sodium nitrite solution, and then mixing with an alkaline solution of H-acid. If no unchanged H-acid is present, no coloration will be produced, as no diazotizable group will be available.

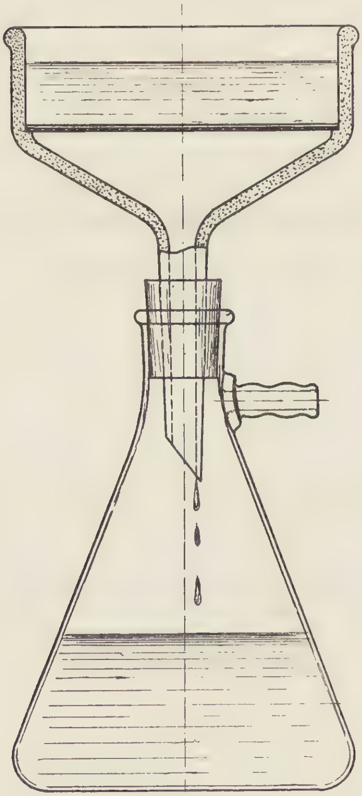


FIG. 22.—Laboratory vacuum filter (Nutsch).

This compound may be coupled with various diazo components to give beautiful azo colours which are very fast to light, and which possess excellent levelling properties ; with diazotized aniline, for instance, the important Aminonaphthol Red G is formed. As the acetyl group is somewhat easily hydrolysed, it is necessary to carry out the coupling with very little soda, and, in addition, to have some ammonia present, which volatilizes when the finished colour is dried, without altering the latter.

9·3 Gms. aniline (1/10 mol.) are diazotized as described, and the diazonium solution is then mixed with the ice-cold acetyl-H-acid, to which 15 gms. of 100 % soda has previously been added. After 1 minute, 20 c.cs. concentrated ammonia are added, drop by drop, and the mass is allowed to stand for 12 hours, after which the dye is salted out in the cold with 20 % of salt, calculated upon the volume of the liquid. The dye is filtered off, well pressed in the screw-press, and is dried at 50°. *Yield about* 50 *gms.*

9·3 gms. Aniline.
15 gms. Na_2CO_3.
20 c.cs. 20 % NH_3.
20 % NaCl.

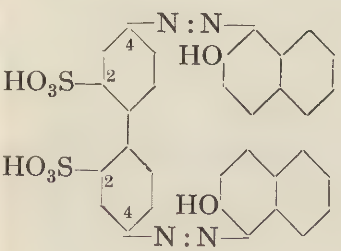
By the use of amino-acetanilide (*cf.* p. 71), the beautiful bluish Aminonaphthol Red 6B is obtained, which is even faster to light than the G brand.

Notes on Works Technique and Practice.—The dyes described have largely displaced the analogues from chromotropic acid (dihydroxynaphthalene disulphonic acid 1:8:3:6), owing to their greater cheapness and fastness to light.

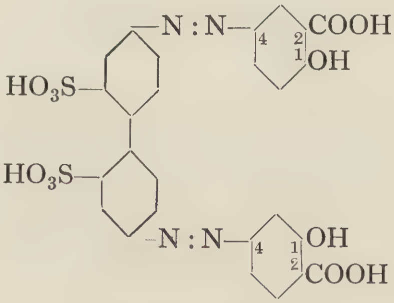
It is of interest to note that it is not feasible to carry out the acetylation on the works in wooden vessels ; if such be used, particularly with pitch-pine, the shade of the finished product is nearly always dull. For this reason the acetylation is carried out in enamel vessels ; in practice, also, a somewhat smaller proportion of acetic anhydride is made use of.

Acid Anthracene Red G and Chromocitronine.

Formulæ :



Acid Anthracene Red G (A.G.F.A.).



Chromocitronine (D.H.).

Benzidine disulphonic acid is so sparingly soluble that it must be diazotized indirectly ; for this purpose it is dissolved in sodium carbonate or caustic soda solution, and the sodium salt mixed with sodium nitrite is run into the acid.

Acid Anthracene Red G.—32 Gms. benzidine disulphonic acid (100 %) are dissolved in 300 c.cs. warm water and 11 gms. soda, and the solution is then mixed with 14 gms. sodium nitrite (100 %)

32 gms. 100 % Benzidine disulphonic acid.

300 c.cs. H_2O.
11 gms. Na_2CO_3.
14 gms. 100 % $NaNO_2$.
60 c.cs. 30 % HCl.
30 gms. β-Naphthol.
30 gms. 30 % NaOH.
50 gms. Na_2CO_3.

at 20°. This solution is allowed to run into a mixture of 60 c cs. of 30 % hydrochloric acid, 200 c.cs. water, and 100 gms. ice ; the temperature may be allowed to rise to 25° without danger. The diazotization is complete in a few minutes. The tetrazo compound is added to 30 gms. β-naphthol dissolved in exactly the same proportions of water, caustic soda, sodium carbonate and ice, as given under Acid Orange A. The further working up is also carried out as given under Acid Orange. It may, however, happen that the tetrazo benzidine disulphonic acid separates out as a sparingly soluble, coarsely crystalline precipitate which will not couple with the alkaline naphthol solution. In this case it is necessary to treat the tetrazo compound at 0° with sufficient caustic soda solution to form the soluble sodium diazotate ; this couples instantaneously with the β-naphthol. Acid Anthracene Red G is fast to milling on wool without the use of mordants.

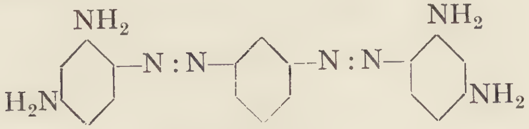
32 gms. Salicylic acid.
80 gms. Soda.

Chromocitronine. (*D.H.*).—The tetrazo solution of the benzidine disulphonic acid is added to a solution of 32 gms. pure salicylic acid dissolved in 80 gms. sodium carbonate and 200 c.cs. water at 5°. After 12 hours the dye which is formed is salted out in the cold with 20 % of common salt, after which it is well pressed and dried at 60°.

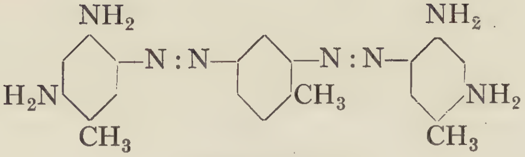
In this case it is unnecessary to redissolve any of the tetrazo compound which may separate out under certain conditions as the Chromocitronine itself goes into solution at once. It is, however, very desirable, especially on a large scale, to filter the solution of the finished colour before salting out, in order that the printing rollers may not become smeared when it is used for calico printing, in which it finds extensive application. The wooden tubs always splinter off to a certain extent, which is liable to cause a good deal of trouble to the printer. Chromocitronine is a beautiful yellow dye, the chrome lakes of which are distinguished by their fastness to light, washing, and chlorine. Owing to its great solubility it penetrates well into the material so that thin fabrics appear to be printed on both sides.

Bismarck Brown G and R.

Formulæ :



Bismarck Brown G.



Bismarck Brown R.

These dyes are mixtures of various colouring matters, in which, however, the products indicated above greatly predominate. The recipes given in the literature on the subject are not very satisfactory, as they always describe the treatment of an acid diamine solution with sodium nitrite. It is, however, far better to acidify cautiously the neutral, mixed solution of the diamine and nitrite, or to allow the neutral mixture to run into the requisite quantity of hydrochloric acid during 12 minutes ; the former method will be described here. Somewhat more nitrite is required than corresponds to the equation :

$$3 \text{ Diamine} + 2NaNO_2 + 4HCl = 1 \text{ Dye} + (2HCl) + 2NaCl.$$

In the case of *m*-phenylene diamine the excess is about 24 %, and in the case of toluylene diamine about 20 %, *i.e.* one uses for 3 mols. diamine, 2 mols. nitrite + 20 % or 24 % excess, respectively. During the formation of the dye the diamine base disappears completely in both cases, as may be seen by salting out a test portion.

Bismarck Brown R (*Vesuvine R*, *etc.*).

36·6 Gms. pure toluylene diamine are dissolved in 1 litre of water at 40°, and after cooling the solution is mixed with 16·5 gms. 100 % sodium nitrite. The volume is then made up to 1600 c.cs. with ice and a mixture of 60 gms. strong hydrochloric acid and 60 c.cs. water is then run in under the surface of the liquid with continuous stirring during 20 minutes. The solution becomes deep brown at once and evolves a fair amount of nitrogen. The end temperature is about 10°. After 8 hours, the product is salted out, with 300 gms. salt, and after standing for 3 hours the mass is filtered, the extremely soluble dye being washed on the filter with its mother-liquor. It is dried at a low temperature (in the works in vacuo), *the dry product weighing about* 50 *gms.*

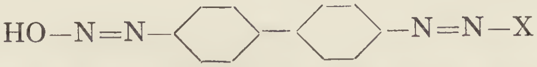
36·6 gms. *m*-Toluylene diamine.
16·5 gms. $NaNO_2$.
1600 c.cs. H_2O.
120 gms. 15 % HCl.
300 gms. NaCl.

The dyeings upon tannined cotton are fast to washing, cheap, and strong, but are not fast to light. In spite of this, however, both brands of Brown are much used for cotton and silk, and especially for leather. Mixed dyeings with Azo Yellow afford good brown shades upon upholstery leather, which are fast to light and rubbing.

The G mark is made in a precisely similar manner, but usually it does not come out in a good crystalline form, and is therefore troublesome to filter ; this disadvantage can be removed to a certain extent by using a larger excess of nitrite.

Benzidine Colours.

Benzidine may be combined with all the phenols and amines which are used for the production of azo colours. It has been found that only one of the two azo groups of tetrazo-benzidine reacts vigorously, the other being relatively inert. In this way it is possible to prepare not only benzidine colours which have a single phenol or amino component, but also in many cases the so-called " mixed " benzidine dyes. Such products, however, are only formed if the first dye component does not react too readily, as otherwise some of the disazo dye will be formed in addition to the intermediate compound :



It would take far too long to mention even the most important types of such intermediate products, so that we must therefore confine ourselves to a few typical examples. Of particular importance is the intermediate compound which is formed by the combination of a single equivalent of salicylic acid with benzidine. This is formed very simply, as a second salicylic group can only be introduced with difficulty after the sodium carbonate coupling by means of an excess of caustic soda solution. Further, it is possible to couple benzidine once with the monoazo dye *p*-nitraniline→H-acid, or with H-acid alone in mineral acid solution without difficulty. Both cases are discussed in detail below.

The Intermediate Compound of Benzidine with Salicylic Acid.

(*o*-Tolidine → *o*-Cresotinic Acid.)[1]

18·6 gms. Tetrazotized benzidine.
15 gms. Salicylic acid.
40 gms. Na_2CO_3.

18·6 Gms. (1/10 mol.) commercial benzidine are tetrazotized as described on p. 110. The clear tetrazo solution is poured rapidly into a solution of 15 gms. pure salicylic acid and 40 gms. anhydrous sodium carbonate, and 300 c.cs. water at 5°. The orange-yellow intermediate compound separates out, and the end of the reaction may be recognized by placing a drop on filter-paper and testing the colourless rim of liquid with alkaline H-acid, when no blue coloration should be given. Stirring is continued steadily until the benzidine reaction has quite disappeared, which will take about 1 hour at 12°.

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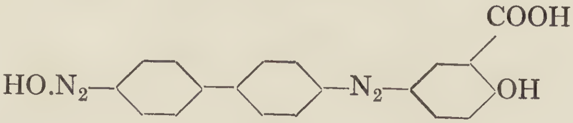
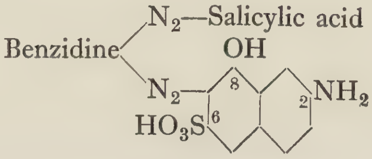
[1] The compound *o*-tolidine → *o*-cresotinic acid is largely made, whereas salicylic acid cannot be used, as the dyes from *o*-tolidine → salicylic acid are very sparingly soluble.

The azo compound, which has the formula :

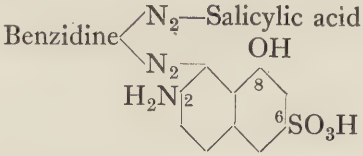


can combine with numerous amines and phenols. Certain of the dyes produced are important. On adding to the intermediate product, for example, a solution of γ-acid made alkaline with sodium carbonate, Diamine Brown V (Cassella) is formed. It is of interest to note that only 85 % of theory of γ-acid is required. If, on the other hand, the intermediate compound is acidified with acetic acid, and is then treated with a solution of γ-acid which is still distinctly acid to litmus, the important Diamine Fast Red F is formed in about 12 hours (at 12–28°), which, owing to the presence of the salicylic acid group, affords chrome mordanted dyeings on wool which are fast to milling.

Formula of *Diamine Brown V :*



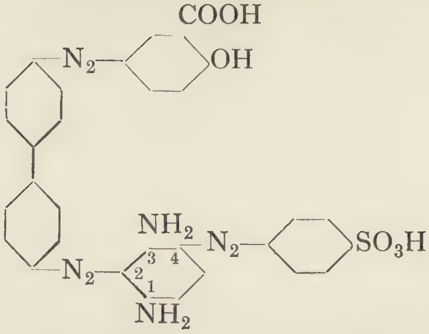
Formula of *Diamine Fast Red F :*



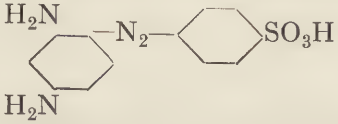
In alkaline couplings the azo group takes up the ortho position to the hydroxyl group, whilst in acetic acid coupling the ortho position to the amino group is attacked.

Dianil Brown 3GN.

Formula :



This dye is one of the most frequently used direct azo colours, as it is extraordinarily strong. It is, however, not fast to acids or light. First of all the monoazo dye *Sulphochrysoidine G* :



is prepared in the following manner : 17·3 gms. (1/10 mol.) sulphanilic acid are diazotized as already described (*cf.* p. 113), and the suspension of the diazo compound, which must be slightly mineral acid, is allowed to drop slowly into a solution of 10·8 gms. purest *m*-phenylene diamine. Preferably the diamine is acidified with 5 c.cs. concentrated hydrochloric acid and the solution made up to 10 % diamine. The coupling is followed by means of alkaline H-acid solution " spotted " upon a filter-paper, and the diazo compound is added until a very faint red colour can be detected on the rim. The diamine base disappears completely, but the true azo colour is not yet formed. After standing for 2 hours at 5°, a 10 % soda solution is run in cautiously with continuous stirring, until the mineral acid has been fully neutralized, about 6 gms. soda being required for this purpose. After standing a further 3 hours at 5°, 5·5 gms. soda are added during 1 hour, and the whole allowed to stand over-night. Next morning a further 10 gms. of sodium carbonate dissolved in a little water, are added, and the whole again allowed to stand for 3 hours. It is most essential to effect the coupling of the sulphanilic acid and the diamine extremely carefully, or else the final colour will be weak. The sodium salt of the Sulphochrysoidine separates out for the most part as a reddish-brown, beautifully crystalline precipitate. The volume of the whole solution

1/10 mol. Diazotized sulphanilic acid.

10·8 gms. *m*-Phenylene diamine.

5 c.cs. HCl.

About 6 gms. Soda.

About 5·5 gms. Soda.

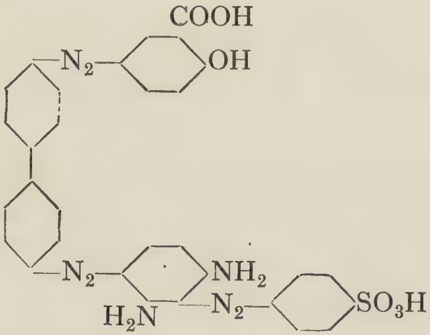
10 gms. Soda.

may be about 500 c.cs., but should not be too dilute. This suspension is mixed at 10° with the intermediate compound benzidine → salicylic acid (*cf.* p. 118), and the mixture stirred steadily for 5 hours. It is then warmed cautiously to 30° and allowed to stand for 12 hours. The liquid is then boiled up and the dye salted out with 200 gms. common salt. It should be a pure brownish red, and should be precipitated in an easily filterable condition; the mother-liquor only contains very little Sulphochrysoidine. *The yield of dry colour is about* 95 *gms.* It will only dye cotton evenly, however, if it is mixed with 10 % of its weight of dehydrated sodium carbonate; too little or too much soda has an unfavourable influence, so that we have here a case similar to that of Direct Deep Black EW (*cf.* p. 118).

1/10 mol. Benzidine-salicylic acid.
200 gms. NaCl.

Notes on Works Practice.—By the use of 1:2:4 toluylene diamine instead of *m*-phenylene diamine an analogous dye is obtained which is, however, somewhat faster to acids. As in this case the para position to the amino group is occupied, it follows that the formula given above for the *m*-phenylene diamine colour is correct, *i.e.* the second azo group is attached between the two amino groups and not in the position para to the NH_2.

If the diamine is first coupled with the benzidine-salicylic acid compound and then with the sulphanilic acid, an isomeric dye is produced of the following formula, which, curiously enough, however, is quite valueless:

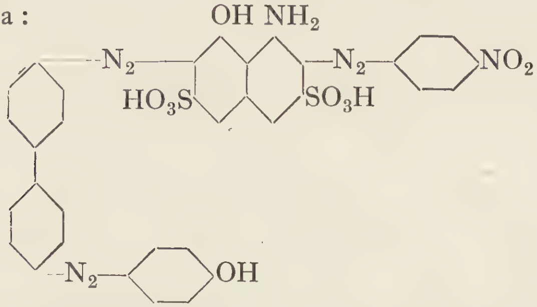


It is very important to use quite pure diamine, as traces of *o*- or *p*-diamine decompose a large portion of the diazo-sulphanilic acid, and also of the intermediate compound, benzidine-salicylic acid. The solution foams up and the dye becomes weak and muddy. By the use of the purest materials the yield is increased by about 40 %, as compared with the impure commercial diamine solution.

The colouring matters from both phenylene and toluylene diamines are used in large quantities for the production of mixed shades.

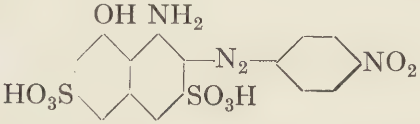
Diamine Green B (Cassella).

Formula :



14·5 gms.
Diazotized
p-nitraniline.
34·1 gms.
100 %
H-acid.
200 c.cs.
H_2O.
5 gms.
Na_2CO_3.
20 gms.
30 %
NaOH.
40 gms.
Na_2CO_3.

14·5 Gms. pure *p*-nitraniline are diazotized as described on p. 109, and to the clear, ice-cold diazonium solution is added 34·1 gms. 100 % H-acid dissolved in 200 c.cs. of cold water and 5·5 gms. sodium carbonate. The addition will occupy about three-quarters of an hour, and care must be taken by means of good mechanical stirring that no lumps are formed. The H-acid combines with the nitraniline in 4–5 hours, setting free an equivalent portion of hydrochloric acid. The mixture is now allowed to stand for at least 12 hours, and next day, after heating up to 50°, 20 gms. of 30 % caustic soda solution are added and 40 gms. soda. The monoazo dye of the formula :

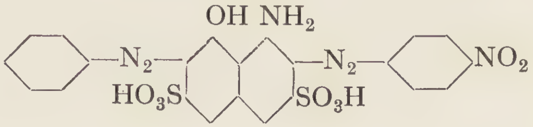


200 gms.
NaCl.

goes into solution with a fine blue colour, and is then salted out by means of 200 gms. common salt. After a few hours, the glistening sodium salt separates out in an easily filterable form, after which it is filtered off and pressed. The mother-liquor has a strong blue colour, but does not yield any further quantity of usable dye on saturating with common salt and is therefore thrown away.

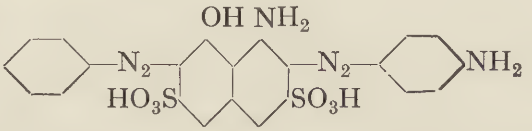
40 gms.
Na_2CO_3.
9·3 gms.
Diazotized
aniline.

If instead of separating out the dye from *p*-nitraniline this is coupled with a calculated quantity of diazotized aniline at 5°, the important *Naphthol Blue-Black B* (C.) is obtained, having the structure :



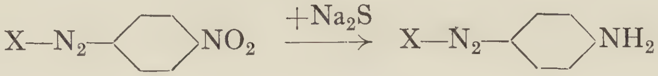
In this case it is unnecessary to isolate the monoazo dye, but an excess of diazotized aniline has a deleterious influence. By salting out at 90° with 15 % of common salt, the Naphthol Blue-Black B is obtained in a fine bronzed form. In passing, it may be mentioned that by reducing Naphthol Blue-Black B with sodium sulphide at 25°, a valuable dark green azo dye is obtained, *Azo Dark Green*, having the following formula :

50 gms. $Na_2S.9H_2O$ 25° C.

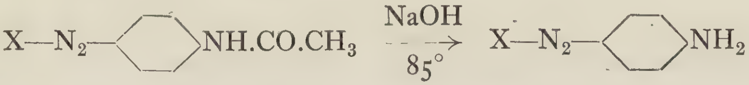


The dye is precipitated out at 50° after standing for 3 hours, with 15 % of common salt and a little sulphuric acid. It is sparingly soluble in bicarbonate ; the mother-liquor is deeply coloured.

The following general rule may be noted : Dyes from paranitraniline may be reduced almost quantitatively to the corresponding *p*-phenylene diamine azo colours by means of the calculated quantity of sodium sulphide :



In this way new amino-azo dyes are obtained which may be again diazotized and coupled up with other components. The same amino-azo dyes may also be obtained by hydrolysis of the corresponding *p*-amino-acetanilide colours.[1]



The sodium salt is dissolved in 500 c.cs. water containing 40 gms. soda at 80°, and is then allowed to cool down to 20° with continuous stirring. Sufficient ice is then added to bring the temperature down to 4° ; a portion of the dye separates out again in a fine state of division. To this suspension is added slowly a solution of tetrazobenzidine prepared as described on p. 110, the solution being added until a drop on filter paper gives a weak but distinct blue coloration on touching the rim with alkaline H-acid solution. At first the discoloration always fades away again, so that a further quantity of the tetrazo solution must be added. Altogether about 18·6 gms.

500 c.cs. H_2O.
40 gms. Na_2CO_3.
About 18·6 gms. tetrazotized benzidine.

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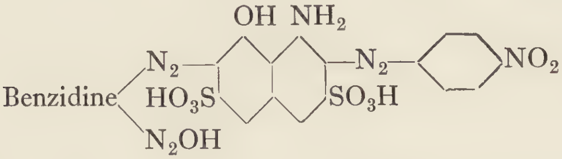
[1] Formyl- and oxalyl-*p*-phenylene diamines may also be utilized.

benzidine must be used, the formation of the intermediate compound taking half an hour.

Formula of the intermediate compound :



12 gms.
Phenol.

About
40 gms.
30 %
NaOH.

150 gms.
NaCl.

About
50 gms.
50 %
H_2SO_4.

300 gms.
NaCl.

12 Gms. of phenol melted up with a little water are added to this compound and left for 3 hours at 10°, after which the temperature is slowly raised to 30°, and the mixture allowed to stand over-night. It is then heated up to 60°, and sufficient 30 % caustic soda-lye added to bring everything into solution (about 40 gms.).[1] 150 Gms. common salt are now added, and dilute sulphuric acid dropped in cautiously until the colouring matter is precipitated (test by spotting on filter paper) ; the latter is filtered off, pressed, and dried at 90°. *Yield about* 110 *gms. strong dye.* Instead of using caustic soda for the separation the product may be heated up to 90° and salted out hot with 300 gms. common salt. The product is not, however, so strong.

Notes on Works Technique and Practice.—In spite of its relatively poor fastness to light, Diamine Green B is one of the most largely used green cotton dyes. It serves for dyeing the cotton layer used for insulating the copper wires for telephone and other cables, and for the production of mixed shades. If salicylic acid be used in place of the phenol, this must be coupled first of all, as it does not combine readily with benzidine when used as a second component. The product so obtained is Diamine Green G, which is, however, much less used as the formation of this colour does not take place so smoothly and, in consequence, the price is considerably higher. In the works, the heating is always effected by blowing in steam, and these dyes cannot be pressed as they are simply forced through the filter-cloths.

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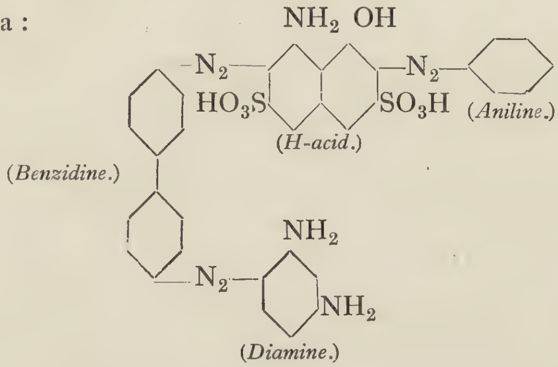
[1] Nitro-azo dyes must not be treated with soda-lye in presence of wood or other reducing substances.

Example of the combination, in presence of Mineral Acid, of an Amine which couples readily, with an Amino-naphthol Sulphonic Acid which couples with difficulty :

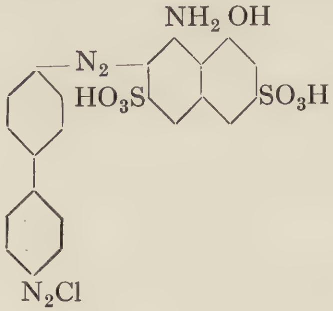
Direct Deep Black EW (Bayer).

Formula :



In the case of Diamine Green B we have become acquainted with a mineral-acid coupling of H-acid with *p*-nitraniline, and have seen that these components combine readily to give a monoazo dye in which the azo group is attached in the ortho position to the amino group. Benzidine couples far less readily, and it is necessary to neutralize continuously the mineral acid which is set free. Contrary to the data given in the patent literature, it is not possible to carry out this reaction in acetic acid solution, since H-acid in presence of sodium acetate at once couples in the ortho position to the hydroxyl. This fact has given rise to many patent actions, which, however, have all been decided in favour of the patentee of the mineral-acid coupling process.

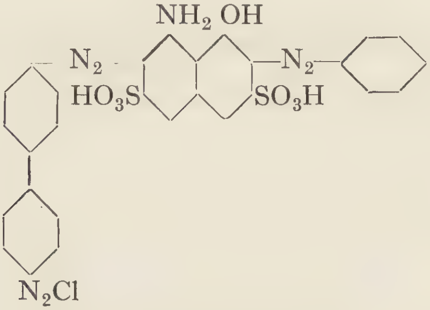
(*a*) The intermediate compound :



19·2 gms. 100 % Benzidine, tetrazotized.
34·1 gms. H-acid.
5·5 gms. Na_2CO_3.
300 c.cs. H_2O.
5·5 gms. Na_2CO_3 in 60 c.cs. H_2O.

19·2 Gms. of 100 % benzidine are diazotized as described on p. 110, and the temperature reduced to 10–12°. To this tetrazo solution is added during the course of an hour the filtered solution of 34·1 gms. H-acid dissolved in 5·5 gms. soda and 300 c.cs. of water. The H-acid solution should react distinctly acid to the litmus. Stirring is continued at 12° for 3 hours, after which a solution of 5·5 gms. soda in 60 c.cs. water is run in very cautiously during 2 hours, care being taken that the mineral acid reaction never disappears for a moment. After a further 3 hours at 12° sufficient dilute sodium carbonate solution is added, if necessary, to give a faint but distinct reaction with Congo paper, the mixture then being allowed to stand all night in a cool place. The reaction for benzidine (with H-acid solution), and also that for H-acid (with diazotized nitraniline), by spotting on filter-paper, will have disappeared completely after 12 hours. The intermediate compound separates out as a powdery precipitate.

(*b*) The intermediate compound :



8·8 gms pure Aniline, diazotized.
26 gms. Na_2CO_3 in 120 gms. H_2O.

8·8 Gms. of pure aniline are diazotized as described on p. 108, and the diazonium solution is added to the first intermediate at 5°, some ice being added if necessary. The mixture is well stirred, and to it is added very rapidly a solution of 26 gms. soda in 120 gms. cold water. It will be seen that everything goes into solution almost instantaneously, after which the new intermediate compound separates out completely. An excess of soda must not be used, or else a portion of the intermediate compound couples up with the H-acid next to the hydroxyl group. The course of the reaction may easily be followed by testing the rim of a spot-test on filter-paper. It sometimes happens that the diazo benzene reaction does not disappear completely, so that the preparation of the final dye is proceeded with after a quarter of an hour.

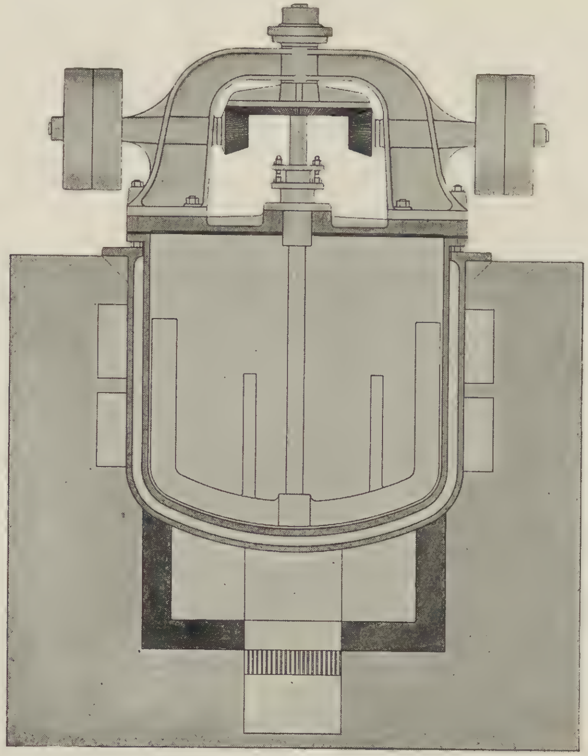


FIG. 29.—Oil-jacketed autoclave with duplex stirring gear for stiff melts (scale 1 : 25).

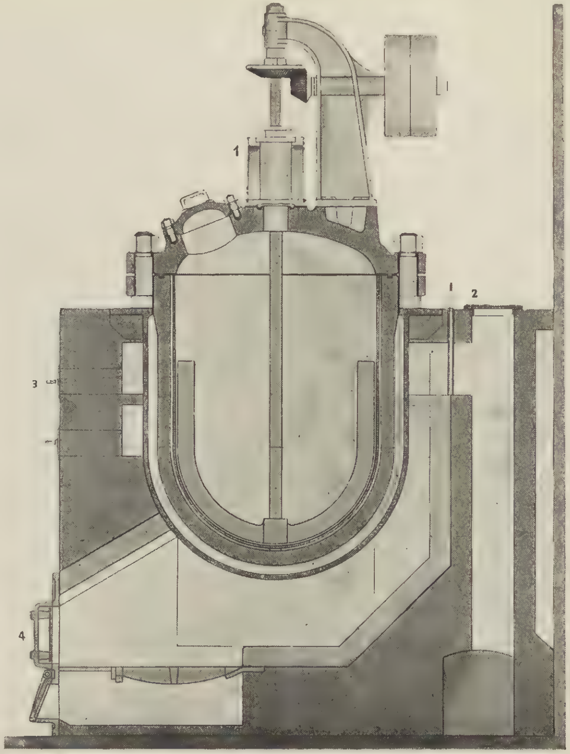


FIG. 30.—Section through an autoclave (scale 1 : 40). 1. Water-cooled stuffing-box. 2. Flue with cover and damper. 3. Flue doors for cleaning. 4. Furnace doors.

To the second intermediate compound are added 11 gms. of purest *m*-phenylene diamine dissolved in a little water, which couples up rapidly with the diazo compound, a portion of the colouring matter formed always going into solution. After 1 hour at 14° the product is heated up cautiously to 50°, and 10 gms. sodium carbonate are added. 120 Gms. salt are then sprinkled in, after which the mixture is acidified with about 20 c.cs. concentrated hydrochloric acid, stirring being maintained until the dye is completely precipitated. It is insoluble in a 10 % solution of common salt and bicarbonate at 50°, so long as it has not previously been boiled up. The product filters very readily and, after pressing, is dried at 100°. *The yield is about* 100 *gms. of strong dye.* To ensure that the dye goes properly on to cotton it must be mixed with 6 % *of its weight of sodium carbonate.*

11 gms. pure *m*-Phenylene diamine.

10 gms. Na_2CO_3.

120 gms. NaCl.

20 c.cs. conc. HCl.

By the use of m-*toluylene diamine instead of phenylene diamine*, Deep Black V is obtained, which possesses a somewhat more reddish shade. In this case also it is necessary to add a little soda after warming up, in order to obtain an easily filterable product.

Notes on Works Practice.—The cotton black just described is the most largely used direct black made in the dye industry. It is used for dyeing all manner of organic materials such as cotton, wool-mixtures, leather, etc. It is prepared in very large azo plants, only the very purest intermediates being employed. By using *m*-phenylene diamine which has been recrystallized from water, the highest yields of colour are obtained, the products dyeing pure black even when the dye-bath is approaching exhaustion. It is included in the so-called " Black Convention " (Schwarz Konvention) concluded between the big colour factories in order to keep the price up to a reasonable level. The price of the most highly concentrated product, which was often only diluted with 3 % of salt and 5 % of soda, was formerly about 3 francs, and even less, per kilo.

Congo Red.

18·6 Gms. of commercial benzidine are diazotized as described on p. 110, and this solution mixed with 50 gms. 100 % naphthionate and 50 gms. sodium acetate dissolved in 200 c.cs. water. The temperature is kept for an hour at 5°, and is then raised slowly to 20°, and kept there for 5 hours. It is then raised to 30°, and stirred for 24 hours at this temperature, which is increased again on the third day to 55°. When the coupling has proceeded for two and a half days, the mixture is boiled up and treated with 40 gms. of

18 6 gms. Benzidine, tetrazotized.

50 gms. Naphthionate.

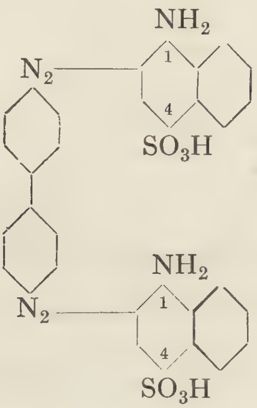
50 gms. Sodium acetate.

40 gms. MgO.

500 c.cs. H_2O.
15 gms. Na_2CO_1.

calcined magnesia, which precipitates out the very sparingly soluble magnesium salt of Congo Red, which is filtered off and thoroughly washed. In this manner the impurities are completely removed. The washed magnesium salt is pasted up with 500 c.cs. of boiling water, and is then decomposed with 15 gms. of sodium carbonate, magnesia being precipitated as carbonate and the dye going into solution as the sodium salt. The hot solution is filtered, the magnesium carbonate washed with water, and the Congo Red precipitated from the filtrate by means of 15 (volume) per cent. of common salt. The colour comes out as a bright red precipitate, and after drying gives *a yield of about* 70 *gms.*

Formula :



Notes on Works Technique and Practice.—In spite of its great sensitiveness to acids, Congo Red, the first benzidine colour to be made, is still largely used, as it is one of the most beautiful of the direct cotton colours. It is only prepared by two or three factories at the present time, as its price no longer allows any profit. The commercial product containing about 60 % of salt costs only about 70 centimes per kilo.

On the large scale, the coupling is often carried out rather differently from the laboratory method. The coupling may be speeded up very considerably by mixing the naphthionate solution with the tetrazo-benzidine solution at 85°, very good stirring being of course essential. Only small charges can be worked up by this method, but, on the other hand, it is possible to effect 8–10 couplings per diem. The excess naphthionate is frequently recovered.

Besides Congo Red, Benzopurpurin is of great importance, and is prepared from *o*-tolidine and naphthionate. In this case it is not possible to carry out the coupling hot, as the tetrazo compound of tolidine is too easily decomposed. This colour is somewhat less sensitive to acids than Congo Red and, like the latter, is largely used in the Orient. It would appear that in the non-industrial countries bordering on the Mediterranean Sea, where the atmosphere is free from sulphurous and sulphuric acids, such dyeings are faster than they are with us.

MISCELLANEOUS AZO DYES.

Tropæoline or Orange IV

(Azo Yellow)

from Sulphanilic acid and Diphenylamine.

The coupling of sulphanilic acid and diphenylamine affords an interesting example of a mineral-acid coupling. In this case it is not possible to work in either neutral or alkaline solution as the diazo-sulphanilic acid is immediately decomposed by sodium carbonate, and in neutral solution it refuses to react, curiously enough. Further, diphenylamine is completely insoluble in water, so that the coupling must be effected in aqueous-alcoholic solution. It is indeed possible under certain conditions, to work without much alcohol, but in this case so much unchanged diphenylamine remains that it becomes difficult to nitrate the dye. Besides Orange IV itself, its nitro derivatives are also valuable. The coupling in alcoholic solution is therefore to be preferred to that in aqueous solution, especially as the yield is better, so that in this way the small loss of alcohol is fully made up for.

As already noted above, diphenylamine has an injurious effect on the nitration, and other impurities which accompany Orange IV possess this property to an even greater extent. If it is intended to convert Tropæoline into Azo Yellow, it is absolutely necessary that the Tropæoline acid shall be quite pure, as slight impurities diminish the yield by 30–50 %. If a pure dye is available, then the actual method of nitration becomes comparatively unimportant. This process is of interest, as the nitro compound is obtained *via* the nitrosamine and nitramine, the Tropæoline being nitrosated with nitrous acid and then oxidized with very dilute nitric acid. The nitramine is formed intermediately, and is then converted at once into the nitro compound under the influence of mineral acid, exactly as Bamberger's phenyl nitramine is transformed into ortho-nitraniline.

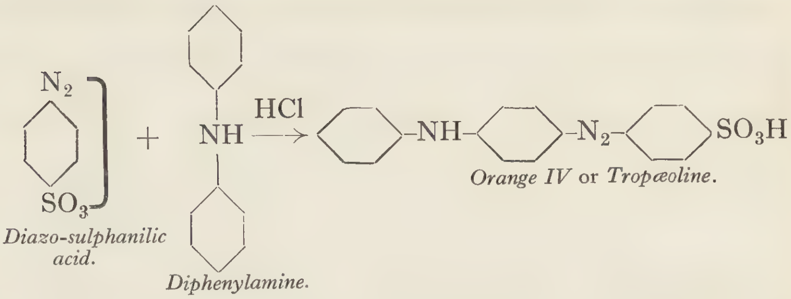
The same relationships are also found in the case of Methylene Green (*q.v.*).

Owing to its pure shade and satisfactory fastness to light and washing, Tropæoline is much used for wool. When mixed with certain dyes it increases their strength considerably. This is particularly the case with the much-used Acid Black 4B (a mixture of about 45 % Naphthol Blue Black B and Naphthylamine Black D, together with 5 % each of Tropæoline and Fast Red AV). Attempts to replace Tropæoline in this case by other yellow colours have shown that the only one having a similar action is Metanil Yellow, which is formed from metanilic acid and diphenylamine. The increase in strength amounts to about 30 %.

For silk, the acid-fast Azo Yellow is used, which goes well on to silk which has been weighted with tin phosphate. For the production of yellow and brown shades fast to water Azo Yellow has become indispensable.

(a) *Tropæoline or Orange IV.*

Reaction :



52 gms. 100 % Sulphanilic acid.
16 gms. Na_2CO_3.
300 c.cs. H_2O.
35 gms. 66° Bé. H_2SO_4.
22 gms. $NaNO_2$.
250 c.cs. 90 % Alcohol.

52 Gms. (3/10 mol.) 100 % sulphanilic acid are dissolved in 16 gms. soda and 300 c.cs. of water, any excess of aniline being boiled off. The solution is filtered off from impurities and is then acidified with 35 gms. concentrated sulphuric acid. The temperature is reduced to 12° by external cooling, after which the liquid is diazotized with 22 gms. sodium nitrite dissolved in a little water. After an hour, the sparingly soluble diazo-sulphanilic acid is filtered off,[1] rinsed out on to the nutsch by means of the mother-liquor, and the crystals pasted up with 250 c.cs. of 90 % alcohol.[2] The mixture

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[1] In a moist condition, diazo-sulphanilic acid is harmless, but when quite dry it is extremely explosive.

[2] The alcohol must not be denatured with pyridine bases ; benzene, however, does no harm.

is cooled to 12° and mixed with 38 gms. of finely divided diphenylamine, no formation of colouring matter taking place. The vessel is then covered with a lid made of cardboard or lead, and 12 gms. concentrated hydrochloric acid are run in with good stirring. The temperature is kept at 12° for one hour, at 14° for 2 hours, and for 2 hours at 18°, the temperature of the water-bath being raised finally to 35°. The dye which splashes on the sides of the pot is washed down again with a little alcohol; no evolution of gas whatever should be noticeable during the entire reaction. If possible, stirring is continued for a further 6 hours, and next day the product is diluted with a litre of water at 50°. The insoluble Tropæoline acid is filtered off and thoroughly washed with water until the washings are a pure yellow. The product is then taken out of the funnel and the curious fact will be noticed that the apparently solid mass becomes completely liquid as soon as it is stirred up; in the works, indeed, this phenomenon is a definite test for the purity of the acid; the more fluid the product is which is obtained from the solid press-cake, the purer is the Tropæoline. The glistening, greyish-blue product is now pasted up with 200 c.cs. of water, boiled, and treated with 30 gms. of potassium carbonate. The beautifully crystalline potassium salt of the dye separates out completely within 24 hours and is then filtered off and dried at 100°. *Yield about 75 gms. concentrated product.* (The sodium salt is sparingly soluble and unattractive in appearance, for which reason it is not very popular with dyers.)

38 gms. Diphenylamine.

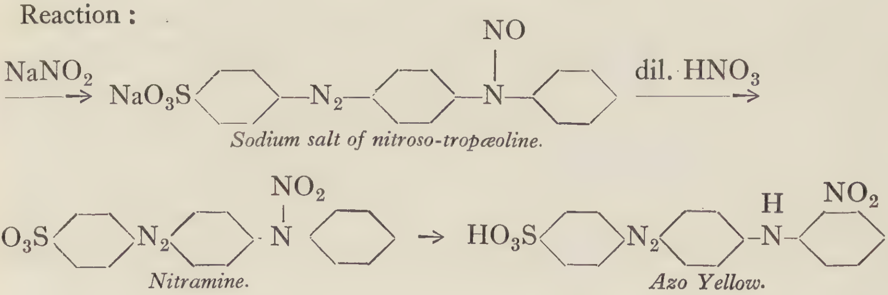
12 gms. 30 % HCl.

200 c.cs. H_2O.

30 gms. K_2CO_3.

(b) *Azo Yellow* (*Indian Yellow*, *Helianthine*, *etc.*).

Reaction :



Sodium salt of nitroso-tropæoline.

Nitramine.

Azo Yellow.

The fresh, well-washed Tropæoline acid is stirred up with 300 c.cs. of water and treated at 5° with 16 gms. of 100 % sodium nitrite. The stirrer must be run very slowly, so as to avoid formation of froth, which hinders the subsequent nitration. After 2 hours the pale

300 c.cs. H_2O.

16 gms. 100 % $NaNO_2$.

40 gms. 60 % HNO_3 (=40° Bé.).
500 c.cs. H_2O.
20 gms $NaNO_2$.
200 gms. NaCl.

yellow nitrosamine has precipitated out, and 40 gms. of 60 % nitric acid are added, stirring being continued for a further 2 hours. The temperature is then increased cautiously to 68°. The product begins to foam, gradually becomes darker, and in 25 minutes all has gone into solution. The liquid is warmed for a further 10 minutes to 71°, after which it is diluted with 500 c.cs. water, neutralized with 25 gms. sodium carbonate, and the Azo Yellow precipitated with 200 gms. salt. The dye separates out in the course of a day as an orange-red granular precipitate, which is filtered off and pressed after 24 hours; drying is effected at 60°, as otherwise decomposition occurs. *The yield is about* 100 *gms.*

The mother-liquor is always strongly coloured, as the nitration never goes quite smoothly, since a certain amount of nitro-diphenylamine and diazo-sulphanilic acid are always formed from the Tropæoline under the influence of the nitric acid. The formation of the diazo compound may be readily recognized if a drop of the nitration mixture be taken at the start and placed on filter-paper, on touching the bright yellow rim with alkaline H-acid solution, the red azo colour from sulphanilic acid and H-acid is at once formed, indeed, in certain factories an impure Orange II (see p. 113) is prepared from the acid mother-liquor.

The Azo Yellow so produced is not sensitive to dilute mineral acids, but does not meet the requirements of silk-dyers for certain purposes. By the energetic action of more nitric acid, greener brands are obtained which are quite fast to acids.

90 gms. 60 % HNO_3.
100 gms. NaCl.
500 c.cs. H_2O.
30 gms. Na_2CO_3.

If it is desired to manufacture the G mark, a process is adopted which differs somewhat from the ordinary. 90 Gms. of 60 % nitric acid (instead of 40 gms.) are taken, and the nitration is begun at 40°. The temperature is raised to 70° during 2 hours and maintained at this point for a further 2 hours, the resultant dye being fast to acid. At the same time it cannot be worked up without further treatment, as it comes out in a slimy form which it is impossible to filter. 100 Gms. salt are therefore added to the nitration liquid, which is diluted to 1 litre and stirred at 70° until the precipitate becomes bright orange and powdery, which takes from 1–2 hours. The liquid is now diluted with 500 c.cs. of water, and then worked up as described for Azo Yellow. *The yield of Azo Yellow G is about* 85 *gms.*

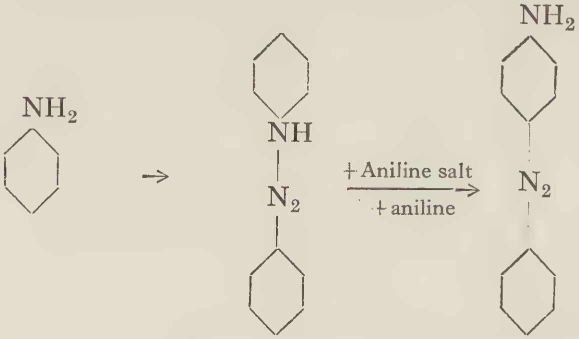
On dissolving in hot water, the nitrated Tropæolines split off nitrous acid, which attacks the copper apparatus used for dyeing. For this reason some dyers demand an Azo Yellow free from nitrous acid, which is prepared in the following manner: the freshly filtered Azo Yellow is heated up to 90° with four times its weight of water, by which means the greater portion of the nitrous and nitric acids are split off. After about 3 hours 5 % of sodium bisulphite is added, which removes the last traces of nitric acid. Red gases are evolved from the mass which foams up somewhat vigorously, for which reason large tubs are required. By this treatment about 15–20 % of the dye is always lost (*cf.* also Azo Flavine FF).

Notes on Works Technique and Practice.—The diazotization and coupling of the sulphanilic acid is effected in large enamelled vessels. The stirrer is often made of thick glass rods which are fixed into a wooden beam, the latter, however, not coming in contact with the liquid. The diazosulphanilic acid is separated on a vacuum filter (see Plate VI.). Instead of an enamelled thermometer tube, one made of bamboo may be used, which lasts a long time. When properly prepared, Tropæoline acid must be quite fluid and capable of being blown out easily from the coupling vessel. After the product has been washed out in the filter-press and thoroughly blown through, the moist Tropæoline acid from 38 kilos. diphenylamine weighs almost exactly 200 kilos. A variation of 10 kilos. more or less shows that impurities are present. The alcohol is recovered, and after neutralizing with soda it is rectified; about 15 % is lost on each operation.

The nitration is carried out in tubs made of pitch-pine, and holding about 2500 litres. They are provided with a good ventilating hood (see Plate VII., Fig. 6), and last for more than a year. The point where the steam, required for heating up, blows into the tub must be protected by means of a board fixed in position with wooden pegs.

Aminoazobenzene from Aniline.

Reaction:



Diazoaminobenzene. *Aminoazobenzene.*

250 gms. Aniline.
110 c.cs. conc. HCl.
45 gms. 100 % $NaNO_2$.
250 gms. H_2O.
250 gms. Ice.
200 c.cs. HCl (approx.).

250 Gms. aniline are mixed with 110 c.cs. concentrated hydrochloric acid in a glass or porcelain beaker with good stirring, after which it is cooled down externally to 32°, and 45 gms. 100 % sodium nitrite, dissolved in a little water, are added at this temperature during half an hour. The temperature must not be allowed to exceed 34°. After 2 hours the temperature is raised to 40°, and after a further hour it is kept for 3 hours at 46°. The mixture is now shaken out into a porcelain basin holding 250 c.cs. of water and 250 gms. ice, concentrated hydrochloric acid being then added until the reaction is distinctly acid to Congo. The excess of aniline goes into solution whilst the sparingly soluble aminoazobenzene hydrochloride remains undissolved ; about 200 c.cs. hydrochloric acid are required. The hydrochloride is filtered off, thoroughly washed with 10 % brine containing 2 % hydrochloric acid, and finally with 2 % hydrochloric acid. The product is dried at 50°, taking care to avoid any over-heating, as otherwise blue-black dyes, the so-called *Indulines*, are formed very readily by internal condensation. *The yield of pure dry aminoazobenzene hydrochloride amounts to about 125 gms.* For the preparation of dyes, the free base is not isolated, the hydrochloride being always used.

Fast Yellow.—Fast Yellow is the disulphonic acid of aminoazobenzene. The first sulphonic group takes up the para position to the azo group, a yellow wool dye being formed which only satisfies very modest demands as to fastness. On the introduction of a second sulphonic group, which is forced to take up the ortho position to the amino group (or azo group), the fastness to light is increased to a remarkable extent.

This sulphonation is carried out very simply : One part aminoazobenzene hydrochloride is added to three times its weight of 25 % oleum with stirring at 25° until a test portion dissolves easily in sodium carbonate. The temperature is then raised to 40°, the stirring being continued, and is heated until a portion dissolves completely in a large excess of water ; this will require about 5 hours. The finished sulphonation mixture is then poured on to six times its weight of ice, after which the mono-sodium salt of the disulphonic acid is salted out with 200 gms. common salt. The flesh-coloured precipitate is filtered off, thoroughly washed with 15 % brine, and the filter-cakes then stirred up with a little water. Sodium carbonate is added at 50° until the colour becomes a pure yellow, a greater or lesser quantity being required according to the thoroughness of the washing. Fast Yellow cannot be salted out, but is evaporated directly to dryness below 90°. *The yield amounts to about 200 % on the starting material.*

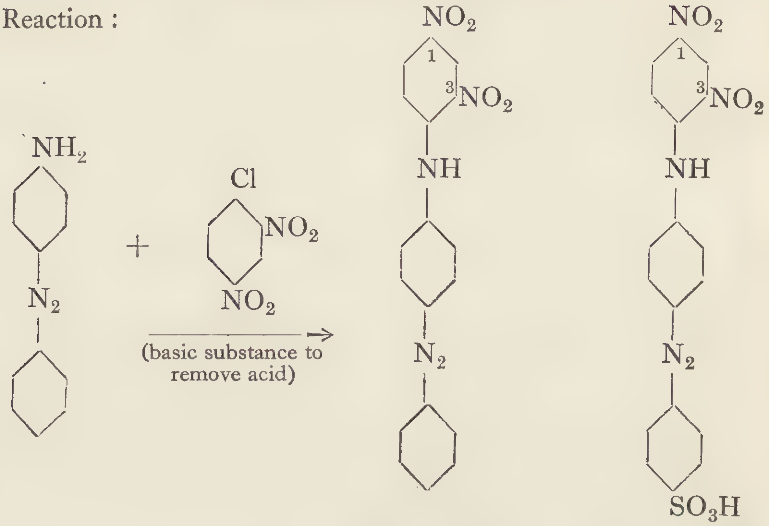
On the large scale aminoazobenzene is prepared in large enamelled vessels holding 300–400 litres. The acidification is carried out in ordinary wooden tubs, and the mother-liquors are worked up for aniline with the aid of line and steam, the loss amounting to about 15 %.

In spite of opinions to the contrary, Fast Yellow is not so fast to light as Tartrazine, and is much less fast than those pyrazolone colours which possess a sulphonic group ortho to the azo group. Aminoazobenzene is an important intermediate for many disazo dyes : if it is diazotized and allowed to act upon phenols, naphthols, and other coupling components, secondary disazo dyes are produced, the earliest of which (aminoazobenzene sulphonic acid → β-naphthol) was the so-called *Biebrich Scarlet*. For this reason such secondary disazo colours are termed dyes of the Biebrich Scarlet type. The diazotization of aminoazobenzene takes several hours ; the freshly prepared aminoazobenzene hydrochloride is suspended in 5 parts of water and a further 150 gms. hydrochloric acid is added for each molecule of hydrochloride. It is also necessary before carrying out the actual diazotization to estimate approximately how much sodium nitrite will be required, by working up a small test portion at great dilution. The diazotization of aminoazobenzene is effected at 10–14°, and often takes a whole day on the large scale. The finished diazotized product is then either worked up at once or cooled down to 0° by means of ice.

Owing to the presence of the amino group, aminoazobenzene may be condensed with dinitrochlorbenzene exactly as is the case with aniline ; the product is Benzene-azo-dinitro-diphenylamine, which is a beautifully crystalline and almost insoluble substance. This can easily be converted into the monosulphonic acid by means of sulphuric acid monohydrate, a nitro-azo dye being produced which has exactly the same empirical formula as Weiler-ter-Meer's Azo Yellow, described on p. 131. It is, however, distinguished from this by its complete homogeneity, and does not split off any nitrous acid on boiling. For this reason some silk dyers prefer it to ordinary Azo Yellow, although its price is somewhat higher.

Azo Flavine FF. (*B.A.S.F.*)

Reaction :



Phenyl-azo-dinitro-diphenylamine. *Azo Flavine FF.*

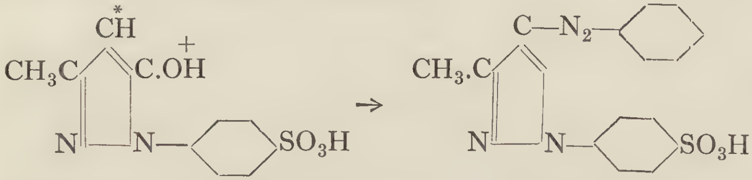
(a) *Condensation of Aminoazobenzene with Dinitrochlorbenzene.*—100 Gms. of 100 % still moist aminoazobenzene hydrochloride, 100 gms. dinitrochlorbenzene, and 250 gms. crystallized sodium acetate are heated up with 600 gms. alcohol (90 %) under a reflux for 6 hours with stirring. The condensation product separates out in the form of reddish brown, glistening crystals which are filtered off hot and washed with a little alcohol. The crystals are dried at 100°, *the yield being about* 115 *gms.*

100 gms. Aminoazobenzene HCl.
100 gms. Dinitrochlorbenzene.
250 gms. Na Acetate.
600 gms. 90 % Alcohol.

(b) *Sulphonation.*—One part of the condensation product is added to three parts monohydrate and stirred for 1 hour at 30°, after which the temperature is raised carefully to 45°. After 1–2 hours a test portion should give a clear solution in dilute sodium carbonate. The product is now poured into six times its weight of water, and the dye is salted out. It is filtered off acid, washed with 15 % salt solution, and then dissolved in a little hot water with the requisite quantity of sodium carbonate. The solution is salted out with 15 (volume) per cent. of salt, a gelatinous precipitate of the sodium salt being first obtained, which, however, soon becomes beautifully crystalline and easily filterable. *The yield from* 100 *gms. condensation product is about* 125 *gms. strong dye.* Azo Flavine FF has the shade of the lower nitrated Tropæolines, and the great resistance to acids of the highly nitrated Azo Yellow.

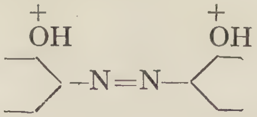
Fast Light Yellow G (Bayer).

Bayer's Fast Light Yellow G is the simplest member of the Pyrazolone series of dyes. These are obtained by two methods, (1) from dioxy-tartaric acid (other α-diketones are also used) and phenyl-hydrazines, (2) from phenyl-methyl-pyrazolones by coupling with diazo components. The second method is simpler, and has therefore largely displaced the older process, although large quantities of Tartrazine (from dioxytartaric acid and phenyl-hydrazine sulphonic acid) are used at the present day. The pyrazolone is prepared from a given phenyl-hydrazine, *e.g.* from the phenyl-hydrazine sulphonic acid described on p. 64, and aceto-acetic ester, which is then coupled with aniline. Reaction :

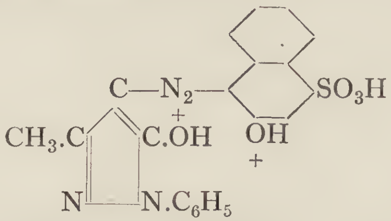


1-*Sulphophenyl-3-methyl-5-pyrazolone.* *Fast Light Yellow G.*

The hydrogen of the phenyl-methyl-pyrazolone sulphonic acid which is replaced during the coupling by the azo group is marked with an asterisk. This hydrogen atom is in the ortho position to an hydroxyl group (+) which renders possible the formation of the coupled product. It behaves exactly like the hydroxy groups in phenols and naphthols, and can bring about lake formation from azo dyes derived from ortho-amino-phenols and ortho-amino-naphthols. Dyes of the following type are produced :



In this manner Erio Chrome Red B (Geigy) is produced from 1:2:4-amino-naphthol sulphonic acid (described on p. 50), and phenyl-methyl-pyrazolone (from phenyl-hydrazine and aceto-acetic ester) ; it is a very fast chrome wool colour :



Erio Chrome Red B (Hagenbach).

19·7 gms. 100 % Phenyl-hydrazine sulphonic acid.
80 gms. 40 % Acetic acid.
13 gms. Aceto-acetic ester.

(a) 1-*Sulphophenyl-3-methyl-5-pyrazolone.*—19·7 Gms. 100 % phenyl-hydrazine sulphonic acid are suspended in 80 gms. of 40 % acetic acid, and to it are added 13 gms. aceto-acetic ester. The whole is then boiled up under a reflux for an hour, and is then cooled down to 15° with continuous stirring, after which the thick magma of crystals is filtered off. *The yield of dry substance is 27 gms. of 90 % pyrazolone.* It is estimated by means of diazotized aniline in acetic acid solution (see Analytical Section).

26 gms. "Pyrazolone."
6 gms. Na_2CO_3.
120 c.cs. H_2O.
30 gms. Sodium acetate.
9·3 gms. Aniline (diazotized).

(b) *Fast Light Yellow G.*—26 Gms. (1/10 mol.) 100 % sulpho-phenyl-methyl-pyrazolone are dissolved in 120 c.cs. water and 6 gms. sodium carbonate, and to this are added 30 gms. sodium acetate. After cooling down to 0° it is mixed with a diazo-benzene solution prepared from 9·3 gms. aniline, and the whole is stirred until a small test-portion precipitated with salt no longer gives a red coloration with alkaline resorcinol solution, which requires from 4–6 hours. The mixture is then boiled up and salted out with 100 gms. common salt. *The yield is about 40 gms. strong dye.*

These Pyrazolone colours, particularly the more complicated ones, are much faster than Fast Yellow (see p. 134). Dyes derived from the ortho-sulphonic acids of aromatic amines such as *p*-toluidine-*o*-sulphonic acid or *p*-chloraniline-*o*-sulphonic acid, include yellow colours which are among the fastest to light with which we are acquainted. The fastness to light can be still further increased by using chlorinated phenyl-pyrazolone for the synthesis of azo dyes, in place of sulphophenyl pyrazolones. An example of this is the *Xylene Yellow* of Sandoz, which is being increasingly used owing to its unexampled resistance to light, despite its relatively high price. There are, of course, almost innumerable possible modifications, of which Geigy's *Polar Yellow 5G* may be instanced. This has the following composition :

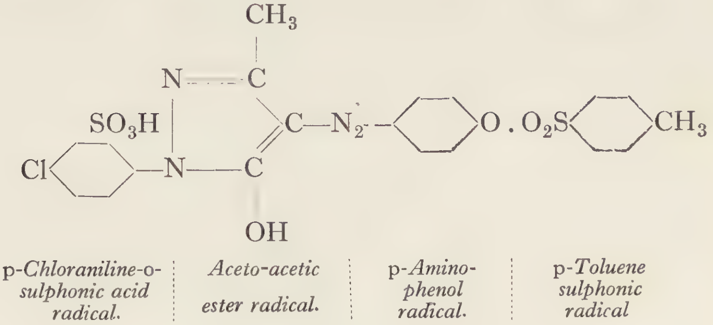

CH3
N
C
SO3H
C—N2—
O . O2S
CH3
Cl
—N——C
OH
p-Chloraniline-o-sulphonic acid radical.
Aceto-acetic ester radical.
p-Amino-phenol radical.
p-Toluene sulphonic radical

PLATE XII.

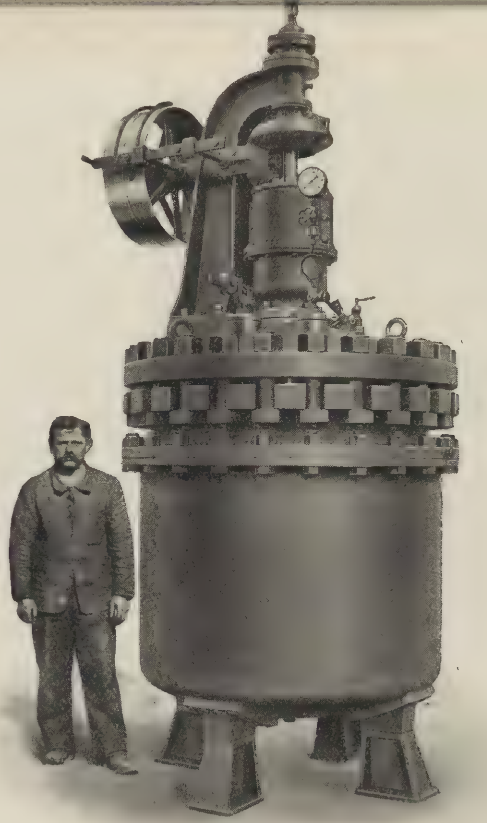


FIG. 31.—Large cast-iron autoclave with steam heating (made by Gebr. Sulzer). Capacity, 1400 litres. Maximum pressure, 25 atms. Owing to the height of the stirring shaft, the water-cooled stuffing-box is easily accessible. At the top, on the right, a tap may be seen, which can be used for removing samples.

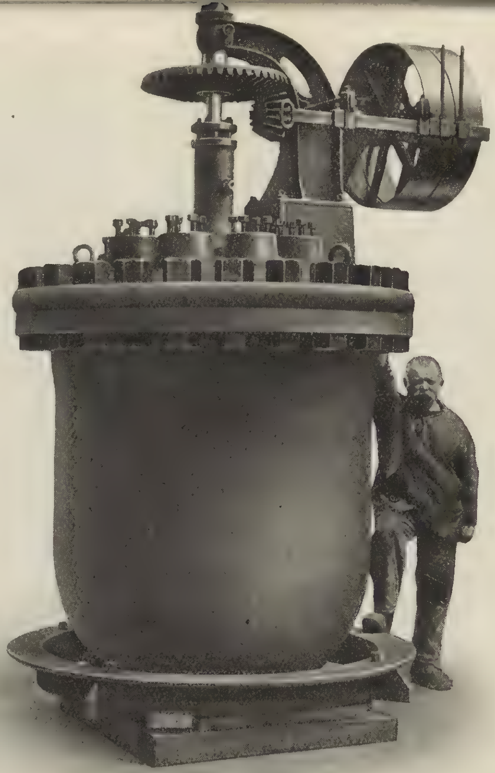


FIG. 32.—Large cast-steel autoclave (made by V. Roll). Capacity, 1500 litres. Maximum pressure, 40 atms. (The stuffing-box is too close to the bracket, which makes it difficult to pack.)

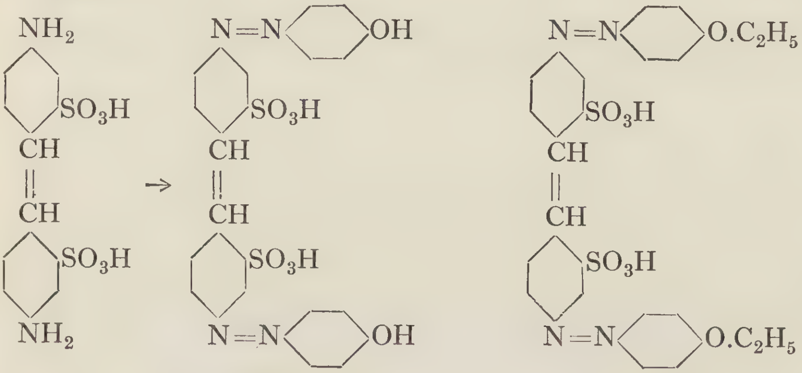
Polar Yellow 5G (Richard); Swiss Cavalry Yellow.

Para-chlor-ortho-sulphophenyl-hydrazine is condensed with aceto-acetic ester, and the resultant pyrazolone coupled with diazo-*p*-aminophenol in acetic acid solution. The azo dye so produced, which is sensitive to alkali, is treated with *p*-toluene sulphonic chloride at 70° in presence of sodium carbonate and 1 molecule caustic soda lye, by which means the hydroxyl group is esterified. As a result of this ester formation the dye becomes quite fast to alkalis, and at the same time fast to milling on wool.

Notes on Works Technique and Practice.—The manufacture of the pyrazolone dyes is simple, the aryl-hydrazines being usually condensed in enamelled vessels so that as little as possible of the expensive substance shall be lost. The diazotization and coupling do not call for special remark.

Chrysophenine G00.

Reaction :



Brilliant Yellow. *Chrysophenine GOO.*

34 Gms. (1/10 mol.) of 100 % diamino-stilbene-disulphonic acid is dissolved in 11 gms. sodium carbonate and 200 c.cs. water, and after cooling the acid is reprecipitated by means of 50 c.cs. (about 60 gms.) of 30 % HCl. The temperature is reduced to 5° by means of ice, and the substance is diazotized during two hours with 14 gms. 100 % sodium nitrite. At the end a slight but detectable excess of nitrous acid should be present. Sufficient ice is now added to reduce the temperature to 0° and then 20 gms. phenol, liquefied with a little water, are added. To the well-stirred suspension of phenol and tetrazo compound is added very rapidly a solution of

34 gms. Diamino-stilbene disulphonic acid.
11 gms. Na_2CO_3.
60 gms. 30 % HCl.
14 gms. 100 % $NaNO_2$.
20 gms. Phenol.

50 gms. Na_2CO_3.
100 gms. NaCl.
About 100 gms. HCl.

50 gms. sodium carbonate dissolved in 200 gms. water.[1] The amount of ice should be so calculated that the temperature after the addition is 8°. All goes into solution, and after a certain time a portion of the Brilliant Yellow precipitates out. After standing for 2 hours, the liquid is heated to 70°, and 100 gms. salt are added, together with enough hydrochloric acid to ensure complete precipitation of the dye, but without causing a change of colour from yellow to blue. After cooling, the product is filtered off and sucked as dry as possible at the pump. It weighs about 180 gms.

Press-cakes 200 gms.
50 gms. Na_2CO_3.
30 gms. 30 % NaOH.
250 gms. Alcohol.
About 40 gms. Ethyl chloride.
About 1 litre 10 % NaCl solution.

Ethylation.—The moist press-cakes are made up with water to 200 gms., and are treated with 50 gms. dehydrated sodium carbonate and 30 gms. of 35 % caustic soda lye. The pasty mixture is placed in a stirring- or rotating-autoclave, and 250 gms. 90 % alcohol are added. The autoclave is charged with 40 gms. ethyl chloride, as described on p. 74, and the mixture is then heated to 100° for 10 hours with continuous stirring (maximum pressure 6 atms.). After cooling and opening the autoclave the contents are diluted with two volumes of 10 % salt solution, and the beautifully crystalline dye is filtered off. Provided that the diamino-stilbene-disulphonic acid was free from diamino-dibenzyl-disulphonic acid, the product is about 20 % stronger than the strongest commercial colour. *The yield is about 70 gms. dry concentrated colour.*

Notes on Works Technique and Practice.—Chrysophenine is the most important direct yellow dye. Owing to its fastness to light upon wool, silk, and cotton, and to its low cost of production, it is almost without a competitor. In addition to the alkylation with aqueous alcohol, the lime method is also of some importance, as in the presence of lime the alkylation may be effected in aqueous instead of in alcoholic solution. In both cases it is essential that the alkyl derivative formed be precipitated at once. Which of the two processes is to be preferred depends upon the current price of alcohol. The alcohol method is better, as it gives directly a finished product of great strength which dissolves to a clear solution, and the pressure during the process does not exceed 6 atms., whereas by the lime method pressures of 25 atms. and over are encountered.

Chrysophenine gives a characteristic reaction with mineral acids, which colours it a beautiful blue. It is of scientific interest to notice that although there are no auxochromes present in the sense of Witt's theory of colour, it is nevertheless an extraordinarily powerful dye.

---

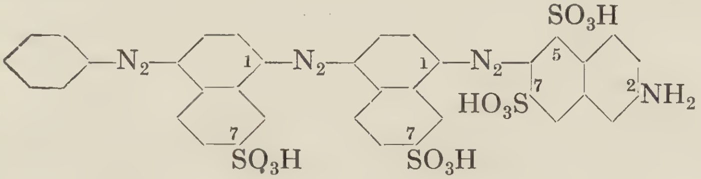
[1] Contrary to the view often held, phenol does not couple at all easily with diazo components. Diazo-ethers are frequently formed, which lead to the idea that a true azo compound has been produced. By carrying out the coupling as described for Brilliant Yellow, *i.e.* by first mixing the mineral acid diazonium compound with phenol (or cresol), and then adding sodium carbonate, but not caustic soda, the azo dye is obtained in far better yield.

The end of the alkylation of the Brilliant Yellow may be recognized in the following manner : a small test-portion is dissolved in water and treated with a few drops of acetic acid. A drop of the faintly acid solution is placed on filter-paper, and the yellow stain is touched with 10 % sodium carbonate solution. As soon as the alkylation is completed no change of colour towards reddish yellow or red should be noticeable. On the large scale samples are taken from time to time by means of a special stop-cock, and the ethyl chloride is not added all at once, but in portions of 10–15 kilos. The heating is done by means of a steam-jacket ; the vessel used is a horizontal rotating autoclave with horizontal stirring gear, the stuffing-boxes of which are kept well cooled, as otherwise the alcohol dissolves out the lubricant at once. The consumption of ethyl chloride is approximately 180 % of theory.

Benzo Fast Blue FR (Bayer)

from Aniline, Cleve-acid and J-acid.

Formula :



The preparation of azo colours of high molecular weight is one of the most difficult in the domain of azo chemistry. It is not possible to lay down general rules, and the following recipe is offered simply as an indication of the methods adopted. It is essential to use pure intermediate products, and the intermediate stages can only be worked up further after a preliminary purification. The dilution is often an essential point, and the sensitiveness to alkalis increases with the molecular weight, whilst the energy with which the coupling takes place rapidly diminishes with the increased size.

Almost all azo dyes of the type :

$$A—N_2—B—N_2—C—N_2—D$$

(*e.g.* Naphthogene Blue 4R ; the combination Naphthylamine-disulphonic acid-2:4:8—Cleve acid-1:7—Cresidine—*p*-Xylidine) dye cotton more or less well without the aid of mordants.

If A is an amine of the benzene series then the dye will be especially fast to light if the para position is replaced by an acetylamino group, or by an oxalylamino group : NH.CO.COOH. Thus *p*-amino acetanilide affords products which are very fast to light. H-acid is also distinguished by the fact that azo colours obtained from it are very fast to light and particularly pure in shade (Benzo Fast Blue FF). In addition many naphthylamine disulphonic acids are of importance in this connection.

As regards B and C there are a large number of possibilities. Cleve acids 1:6 and 1:7 are used, and also *m*-toluidine, which differs from aniline in coupling readily with azo components. *m*-Amino-*p*-cresol methyl ether, the so-called " Cresidine," is much used, as dyes containing this component possess great purity and strength.

As to D two compounds are of special importance, namely aminonaphthol sulphonic acid 2:5:7 (J-acid) and *p*-xylidine. Colours derived from *p*-xylidine may be diazotized further on the fibre, and unite with naphthols and amines to yield products which are fast to light and washing.

As may be seen from these indications the possibilities are almost unlimited. More than a hundred dyes of this type are met with in commerce, and every colour factory places both patented and free products on the market.

(a) *Aniline-Cleve acid*-1:7.

9·4 gms. diazotized Aniline and Na formate.

22·3 gms. 100 % Cleve acid 1:7.

25 gms. Na formate.

9·4 Gms. pure aniline are diazotized as described on p. 108, and the diazonium solution is neutralized by means of sodium formate, which is cheaper than the acetate, until it is just mineral acid. The neutralized solution is added to 22·3 gms. Cleve acid 1:7 dissolved in 300 c.cs. water, using the pure sodium salt of the latter. As soon as the solutions have been mixed, a further 25 gms. sodium formate in concentrated solution are added, which has previously been made faintly acid to litmus by means of formic or acetic acids. The aniline combines with the Cleve acid at 8° within 5 hours, but it is advisable to allow the coupling to stand all night, as this is the only way of ensuring that a uniform dye will be produced. Next day 20 gms. caustic soda lye (30 %) is added, and the mixture allowed to stand for at least 4 hours at 20°. (It is a great mistake to try to work up such couplings too quickly.) A valueless azo colour is produced which must now be diazotized further in a special manner.

20 gms. 30 % NaOH.

(b) *Aniline-Cleve acid*-1:7—*Cleve acid*-1:7.

The suspension of the orange-yellow monoazo dye is treated with 60 gms. common salt and 7·5 gms. sodium nitrite. Sufficient ice is then added to reduce the temperature to 0°, after which 50 c.cs. concentrated hydrochloric acid are quickly added; the reaction should be distinctly mineral-acid. In the present case the diazotization can be carried out only in presence of sodium chloride, and it is necessary to precipitate out the sodium salt of the colouring matter in the presence of NaCl and of nitrite, as otherwise the diazotization is almost impossible. A similar case was discussed when dealing with the diazotization of α-naphthylamine (see p. 109).

60 gms. NaCl.
7·5 gms. $NaNO_2$ (100 %).
Ice, to 0°.
50 gms. 30 % HCl.

The temperature may be allowed to rise to 12°, and the diazotization is to be regarded as complete when nitrous acid can be distinctly noticed after 2 hours.[1] If necessary, a little sodium nitrite may be added. The mixture is allowed to stand all night at 10–12°, and the brown diazo compound is filtered off quickly on a large nutsch. Although it is quite stable, it must be protected from heat and light. The mother-liquor is deeply coloured and is thrown away.

The diazo compound is now stirred up with 400 gms. ice-water to a thin paste, which is then mixed with 22·3 gms. Cleve acid and 20 gms. sodium formate, exactly as described for the first coupling. The mixture is stirred for 6 hours at 5–7°, and is then allowed to stand over-night, after which it is heated up to 50° and allowed to stand a further hour at this temperature. 25 Gms. of 30 % caustic soda solution are then allowed to drop in during one hour, the dye going into solution with a blue-violet colour. Unfortunately it is not possible to salt out the dye from the alkaline solution, which must be acidified. At the same time, however, various impurities are also precipitated which are carried along and accompany the finished product. After the addition of 100 gms. of salt, the product is acidified with about 50 c.cs. of 15 % hydrochloric acid, after which the dye is filtered off, pasted up with 200 c.cs. water and 25 gms. caustic soda, and completely dissolved up at 90°. 7 Gms. of 100 % sodium nitrite are added to the liquid, and the clear solution is then allowed to run into a mixture of 60 gms. of 30 % hydrochloric acid, 400 gms. ice, and 300 c.cs. water, at 60° during half an hour. Ice

400 gms. Ice-water.
22·3 gms. 100 % Cleve acid 1:7.
20 gms. Na formate.
25 gms. 30 % NaOH.
100 gms. NaCl.
50 gms. 15 % HCl.
200 c.cs. H_2O.
25 gms. NaOH.
7 gms. 100 % $NaNO_2$.
60 gms. 30 % HCl.

---

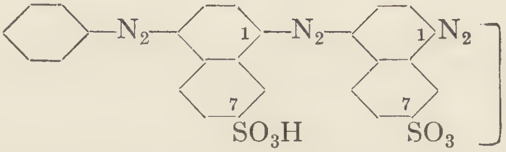
[1] Such diazo compounds are deeply coloured, and it is usually not possible to test them directly for nitrous acid by means of nitrite paper. A drop, therefore, of the solution or suspension which is to be examined is placed on a little heap of salt lying on thin filter-paper. The coloured substance is precipitated out by the salt, and by pressing the reagent paper on to the reverse side of the filter-paper it can readily be seen if mineral acid and nitrous acid are present in excess.

400 gms. Ice.
300 c.cs. H_2O.

is added fast enough to keep the temperature constant at about 8°. The total volume at the end should be about 1½ litres, and, if a pure Cleve acid-1:7 has been used, a completely clear solution of the diazo compound will result; this again cannot be precipitated, as it decomposes readily.

(c) *Aniline—Cleve acid—Cleve acid—*J-*acid.*

The clear, deeply coloured solution of the diazo compound which has the formula:



20 gms. 2:5:7-acid (100 %).
60 gms. Na_2CO_3.
300 c.cs. H_2O.
150 gms. NaCl.

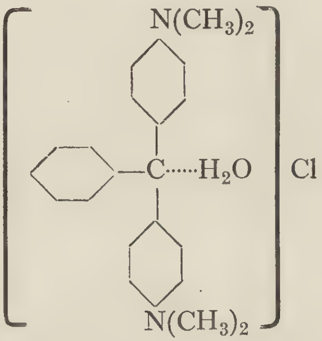
is allowed to drop during one hour into a solution of 20 gms. of 100 % J-acid (aminonaphthol sulphonic acid 2:5:7), 60 gms. soda, and 300 c.cs. water. The temperature must not exceed 0°, and must be regulated by means of ice. Stirring is continued for an hour, and next day the mixture is boiled up in a porcelain basin. 150 Gms. salt are then added, and the precipitate filtered off at 80°. The mother-liquor is highly coloured and always contains a certain amount of J-acid. It is not feasible to diminish the excess of J-acid, as by so doing the yield of colour is diminished in proportion. The precipitate filters slowly, but is obtained finally almost free from salt, as it is in a good crystalline condition. It is again treated with a little 5 % brine, and is then dried at 100°, the resultant product forming a fine bronzed powder *weighing about* 40 *gms.* Benzo Fast Blue FR dyes cotton in blue shades which are fast to light and are superior to those obtained from Indigo. The fastness to chlorine, however, is very slight, and the fastness to washing only moderate. Whether the preparation has been carried out properly may be determined not only from the yield, but also from the exhaust. A correctly made dye will give exhausts of the same shade as the original dyeing, though of course correspondingly weaker.

Notes on Works Technique and Practice.—Dyes of this class are manufactured in ordinary azo-colour sheds as indicated diagrammatically on Plate VII. Owing to the instability of the diazo-compounds it is necessary to use very large filter-presses so that the whole charge may be put through in one operation. It is then possible to work up the diazo compound immediately after emptying the filter-press. It is also advisable to manufacture this colour during the colder season of the year, and to allow only very trustworthy men to deal with the operation. Again, it is a very good plan, whenever possible, to carry out in the laboratory the next operation, with a small portion of the intermediate product (*e.g.* 1/1000th part), before the actual manufacturing stage is begun ; by this means many disappointments will be avoided. The various intermediate products should also be kept as samples in a pure form so that by careful comparison one may judge whether the process is pursuing a normal course.

7. *TRIPHENYLMETHANE DYES*

Malachite Green.

Formula.[1]



(a) *Leuco-Malachite Green.*

37·8 Gms. (3/10 mol.) dimethylaniline, 24 gms. (2/10 mol.) 30 % hydrochloric acid, and 10·6 gms. (1/10 mol.) benzaldehyde are placed in a 300 c.c. bolthead and the mixture heated up for 12 hours with a reflux-condenser. To prevent the oxidation of too much aldehyde, the end of the condenser is closed with a plug of cotton-wool. It is necessary to stir vigorously during the whole reaction. At the end of this time the benzaldehyde will have disappeared almost completely. 12 Gms. anhydrous sodium carbonate are added, and the excess of dimethylaniline is driven off with steam, and may be readily recovered. The residual leuco base of Malachite Green is separated from the water after cooling, powdered, and again washed. *The yield of dry product is about 24 gms.*

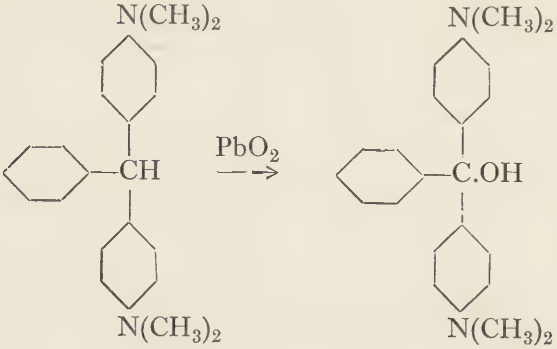
37·8 gms. Dimethylaniline.
24 gms. 30 % HCl.
10·6 gms. Benzaldehyde.
12 gms. Na_2CO_3.

---

[1] The formula of Malachite Green is given here in accordance with the scheme put forward in *Helvetica Chimica Acta*, 1918, part 3.

(b) *Oxidation of Leuco Base to Colour.*

Reaction :



Oxidation is effected in dilute aqueous solution with the exactly calculated quantity of lead peroxide (see analytical section). On the laboratory scale it is possible to obtain a lead peroxide paste of exact composition, without resorting to analysis, by dissolving a weighed portion of lead nitrate in water and treating with calcium hypochlorite solution until all the lead is precipitated.[1] The precipitated peroxide is then washed with plenty of water and used as a moist paste.

16·5 gms. Leuco base.
300 c.cs. H_2O.
20 gms. 30 % HCl.
+Ice.
11·9 gms. PbO_2.
25 gms. Na_2SO_4, or
10 gms. 66° Bé. H_2SO_4.
15 gms. Na_2CO_3.

16·5 Gms. (1/20 mol.) pure leuco base are dissolved in 300 c.cs. water and 20 gms. strong hydrochloric acid, and the solution made up to 400 c.cs. at 0° with ice. The liquid is well agitated and to it is added quickly a peroxide paste from exactly 1/20th molecule lead nitrate (=15·5 gms.). After 2 hours a solution of 25 gms. Glauber salt is added, the lead being precipitated as the insoluble sulphate, which is removed by filtration. The colour base is now precipitated by means of 15 gms. anhydrous sodium carbonate, and is filtered off; usually it comes out in a resinous form. *The yield of dry product is about* 16 *gms., or almost* 100 % *of theory.*

(c) *Crystallization of Malachite Green.*

120 gms. "Base."
72 gms. cryst. Oxalic acid.
300 c.cs. H_2O.

It is not easy to effect the crystallization in the laboratory as large quantities are required for the production of fine crystals. 120 Gms. base (or, better, several times this amount) are dissolved in 72 gms. crystallized oxalic acid and 300 gms. distilled water, and the impurities filtered from the boiling liquid. A very concentrated solution of 7 gms. ammonium oxalate is then added to the hot liquid, and the mixture allowed to stand away from draughts. The best plan is to place the vessel containing the solution inside another larger vessel filled with hot water, so as to allow the former to cool down slowly. The temperature is now allowed to cool during the course of a day to 70°, when the fine crystals are filtered off. A further quantity of less pure dye separates out from the mother-liquor on cooling, and forms the Malachite Green II. of commerce. *The yield from one part of leuco base may be up to* 1·45 *parts oxalate or* 145 % *by weight of the initial material.*

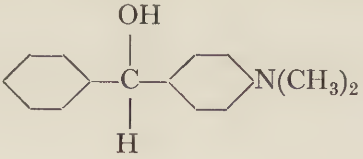
---

[1] Calcium hypochlorite is very soluble, like calcium chloride; the insoluble residue, after treating with water, consists of lime and chalk. All heating must be avoided.

7 gms. $(NH_4)_2.C_2O_4$

Notes on Works Technique and Practice.—Malachite Green is still a very important product, and serves for dyeing tin-weighted silk, wool, and paper. Mixed with other dyes, it yields pure mixed shades which are very cheap, but possesses only moderate fastness. It is also used for printing on silk and cotton, but for these purposes its fastness is not adequate to modern demands, so that its use is diminishing.

The condensation is effected nowadays only with mineral acid, the old zinc chloride method having long been given up ; Doebner's method, also, starting from benzotrichloride, is no longer utilized. The condensation is effected by means of hydrochloric or sulphuric acid. Hydrochloric acid effects the condensation more quickly, but requires the use of enamelled apparatus, whilst the sulphuric acid condensation may be carried out in homogeneously lead-lined vessels. It is important not to use too much acid or else the condensation goes to a certain extent in another direction, a benzydrol of the following formula being produced as a by-product :



which is, of course, incapable of giving the required dye by oxidation.

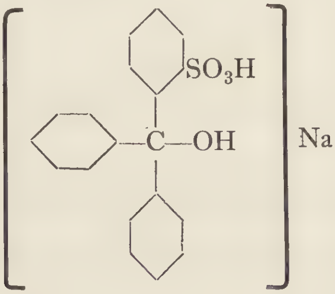
Various fractions are obtained when working on the large scale, as different customers demand products of varying appearance. The oxalate of Malachite Green has the formula

$$2 \times C_{23}H_{24}N_2 + 3 \times C_2H_2O_4.$$

The crystallization may occupy several days when working with quantities of from one to six cubic metres, and crystals are frequently obtained of considerable beauty. The addition of ammonium oxalate to start the crystallization is reminiscent of similar relationships in alkaloid chemistry and is a purely empirical discovery. For further details see under Xylene Blue.

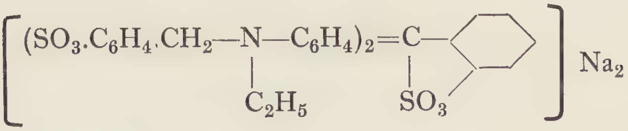
Xylene Blue VS (Sandoz).

Xylene Blue belongs to the so-called Patent Blue class, which includes sulphonated triphenylmethane dyes which are fast to alkalis. These products all have the common factor that the sulphonic group is in the ortho position to the methane carbon atom. The general formula is therefore :



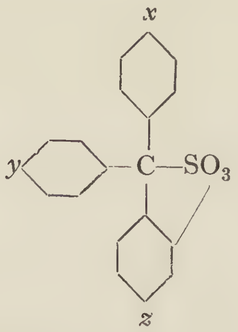
Sandmeyer was the first to recognize the connection between constitution and stability to alkalis, and his Erioglaucine, the formula of which is given below, was the first colour to be prepared in the light of this important knowledge :

Erioglaucine (Sandmeyer).



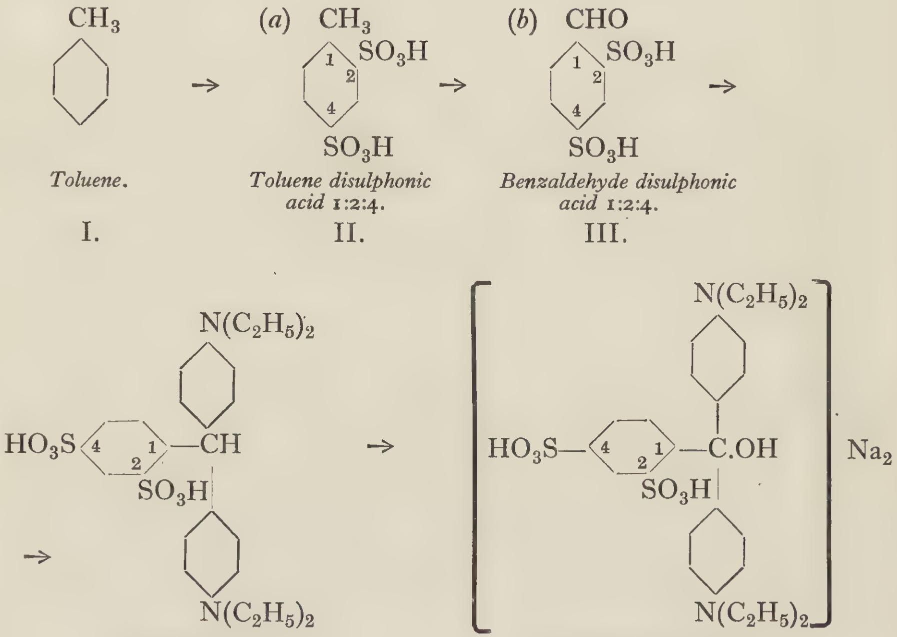
from Ethylbenzylaniline sulphonic acid and Benzaldehyde orthosulphonic acid.

Probably an internal anhydride is formed between the carbinol hydroxyl and the sulphonic group, and to this is due the great stability towards sodium carbonate and caustic soda. This hypothesis is not a mere wild guess, but is strongly supported by the fact that dyes of the formula—



are quite insoluble in alkalis.

Reaction :


CH_3
(a) CH_3
SO_3H
1
2
4
SO_3H
(b) CHO
SO_3H
1
2
4
SO_3H
$N(C_2H_5)_2$
HO_3S
4
1
2
—CH
SO_3H
$N(C_2H_5)_2$
$N(C_2H_5)_2$
HO_3S—
4
2
1
—C.OH
SO_3H
$N(C_2H_5)_2$
Na_2

Toluene. I.

Toluene disulphonic acid 1:2:4. II.

Benzaldehyde disulphonic acid 1:2:4. III.

Leuco-Xylene Blue VS. IV.

Xylene Blue VS (Steiner). V.

(a) *Toluene disulphonic acid.* II.

46 Gms. pure toluene ($\frac{1}{2}$ mol.) are mixed with 80 gms. sulphuric acid (monohydrate) by dropping the acid into the boiling toluene during a quarter of an hour and then heating to 125° for an hour. The toluene will have completely disappeared by this time, and the

46 gms. Toluene.
80 gms. 100 % H_2SO_4.

220 gms. 66 % Oleum.

400 gms. 66 % H_2SO_4.

mixture is then cooled down to 30°, after which 220 gms. of 66 % oleum is run in during half an hour. The product is heated up to 125° for 4 hours, all the toluene being thereby converted into the disulphonic acid. The mixture is then diluted with 400 gms. of sulphuric acid (66° Bé.) and the whole transferred to a porcelain pot provided with a good iron stirrer.

(b) *Benzaldehyde disulphonic acid.* III.

100 gms. MnO_2 as Mn_3O_4.

The product is treated by degrees with 125 gms. 80 % manganese paste in small portions, with good stirring.[1]

Approx. 25° gms. CaO.

The addition should occupy half an hour, the temperature of the mixture being about 25°. When the addition is completed, the product is stirred for a further 3 hours at 30°, and the temperature is then raised to 120°. At this temperature the mixture usually becomes so thick that stirring is impossible. The dark colour of the manganese dioxide gradually changes to a pale grey. It is rarely possible in the laboratory to effect the oxidation so completely that all the dioxide disappears, and it is necessary to stop the reaction before this point is reached. After standing for 12 hours the mass is diluted with 2 litres water and slaked lime added until the mineral acid reaction has completely disappeared.

About 50 gms. Na_2CO_3.

Litmus, however, should not be turned a pronounced blue, as any excess of alkali destroys the aldehyde sulphonic acid. The pasty mass of calcium sulphate is now treated with strong sodium carbonate solution until a filtered test-portion no longer gives a precipitate on adding sodium carbonate. The solution is filtered from the calcium sulphate and manganese, the precipitate well washed, and, if possible, the gypsum again pasted up with water and filtered. The faintly alkaline filtrate is evaporated down in vacuo to 250 c.cs., and is then filtered, if necessary, from any traces of calcium sulphate or manganese oxide. The yield may be estimated by treating an aliquot part of the solution in presence of sodium acetate with a solution of phenyl hydrazine acetate of known strength until a portion, after salting out, no longer reacts on a further addition of "hydrazine." With this reagent an intense yellow coloration is at once produced ; the method of estimation is not very accurate, however.

---

[1] The manganese paste is calculated as MnO_2, *i.e.* exactly 100 gms. of manganese dioxide is used in the form of the so-called "Manganese Mud," which is a waste product from the manufacture of saccharine and possesses the approximate formula Mn_3O_4. For estimation, see Analytical portion.

PLATE XIII.

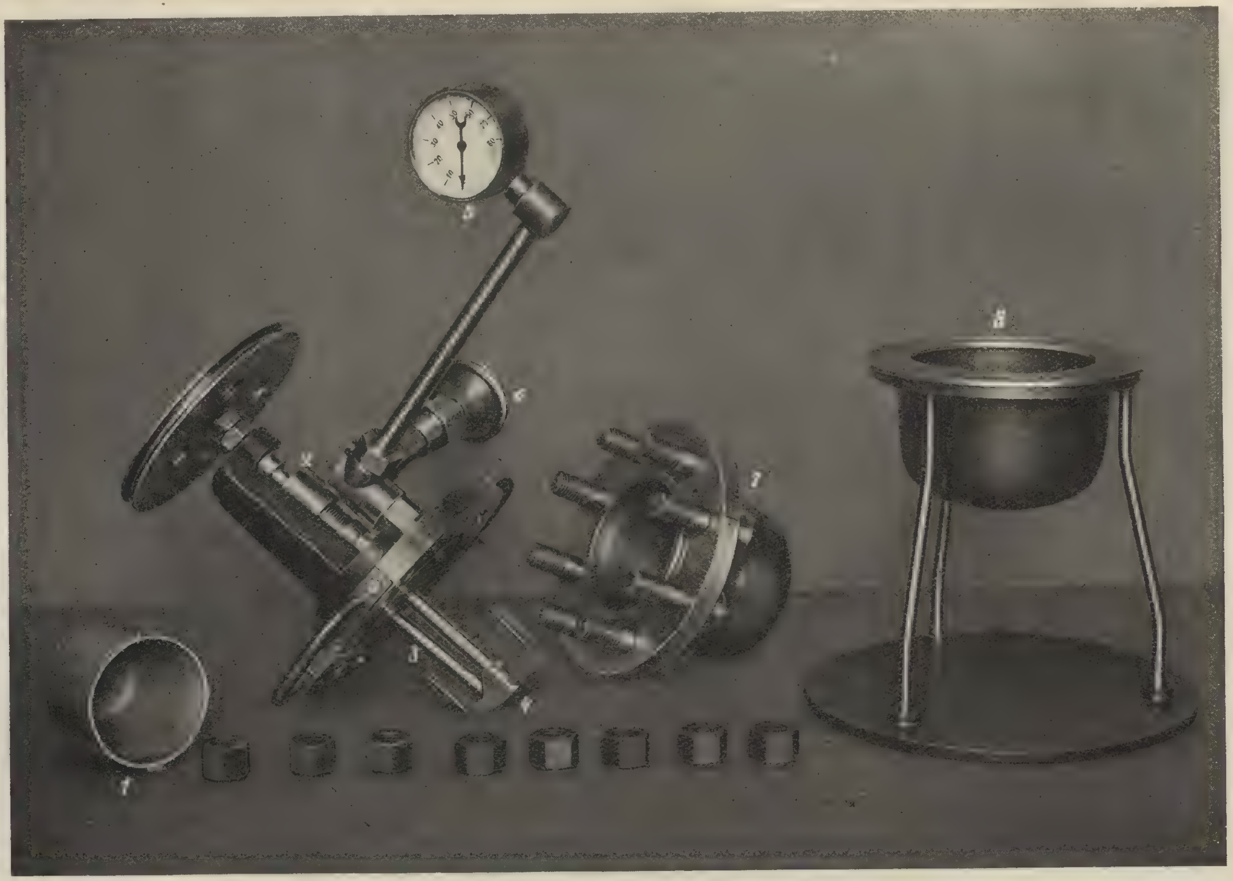


FIG. 33.—The stirring autoclave shown in Plate I., taken apart. 1. Liner to fix in with solder. 2. Stuffing-box. 3. Thermometer tube. 4. Stirrer. 5. Manometer. 6. Valve. 7. Body of autoclave with bolts. 8. Copper oil-bath with iron ring.

(c) *Condensation to leuco compound.* IV.

The whole solution is boiled up with 45 gms. sulphuric acid and 100 gms. pure diethyl aniline for two days under a reflux, after which the mixture is made alkaline by means of 100 gms. 30 % caustic soda lye, and the excess of diethylaniline is driven off with steam. If necessary the alkaline solution is filtered and is then made just acid with 50 gms. concentrated sulphuric acid. The internal anhydride of the leuco compound is precipitated in the course of 24 hours as fine white needles, which are filtered off and thoroughly washed out with water. After drying thoroughly at 80° they weigh 70 gms.

45 gms. H_2SO_4, 66° Bé.
100 gms. Diethylaniline.
100 gms. 30 % NaOH.
About 50 gms. conc. H_2SO_4.

(d) *Oxidation to the Dye.* V.

The oxidation closely resembles that for Malachite Green. 50 Gms. of the leuco compound are dissolved in a *boiling* solution of 8 gms. anhydrous sodium carbonate, as the sparingly soluble leuco compound is practically insoluble in cold soda solution. The liquid should be perfectly neutral to litmus, and is made up to 1800 c.cs. at 0°. A mixture of 15 c.cs. concentrated sulphuric acid and exactly 22 gms. 100 % lead peroxide paste is added in one operation to the mixture (*cf.* Malachite Green).

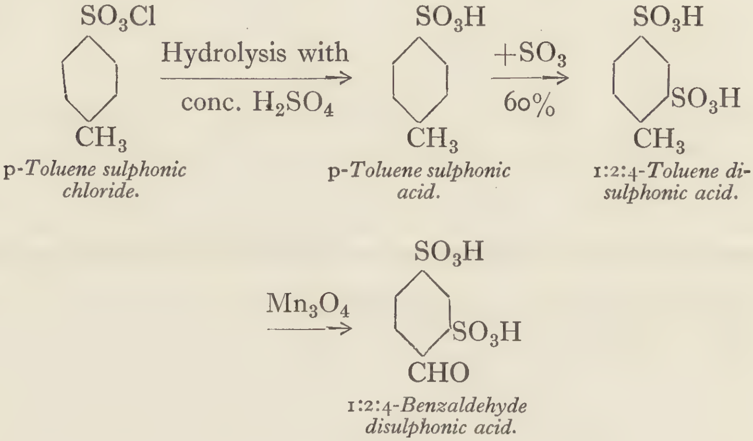
50 gms. Leuco compound.
8 gms. Na_2CO_3.
15 gms. conc. H_2SO_4.
22 gms. PbO_2 100 %.

After standing an hour at 0–5° the product is heated to 80° and the lead sulphate filtered off. The solution is evaporated down to 150 c.cs., preferably in vacuo, and 50 gms. salt are added. The finished dye, which comes out in a beautifully crystalline form during the course of a day, is filtered off and washed with a little saturated brine. It is then dried in a small porcelain basin, after adding a drop of ammonia to neutralize any remaining trace of mineral acid.

Yield of concentrated dye = 32 gms.

Notes on Works Technique and Practice.—The benzaldehyde disulphonic acid is so easily soluble that it is not possible to isolate it. The oxidation is effected in large kneading troughs with interlacing arms such as were first built by Werner and Pfleiderer. The apparatus may be heated by means of a steam jacket, and owing to its powerful construction the mixing may be continued right up to the end. By this means it is possible to work with rather less sulphuric acid than indicated above. Liming and evaporation are carried out by known methods, but one difficulty shows itself. The heating tubes become very quickly encrusted with calcium sulphate, and owing to the sensitiveness of the aldehyde disulphonic acid it is not possible to use any excess of soda in order to precipitate the lime completely. The condensation is carried out in homogeneously lead-lined stirring autoclaves, whilst the oxidation is done in wooden vats provided with propeller stirrers constructed of ash. The evaporation is performed in vacuo, and the separation of the well-crystallized colouring matter is done by centrifuging. On treating the mother-liquor with aniline an impure dye is formed which constitutes the Mark II. of commerce.

More recently the 1:2:4-benzaldehyde disulphonic acid is often made from *p*-toluene sulphonic chloride instead of from toluene. Owing to this and other uses for the substance the once almost valueless sulphochloride has risen considerably in price.



p-*Toluene sulphonic chloride.* p-*Toluene sulphonic acid.* 1:2:4-*Toluene disulphonic acid.*

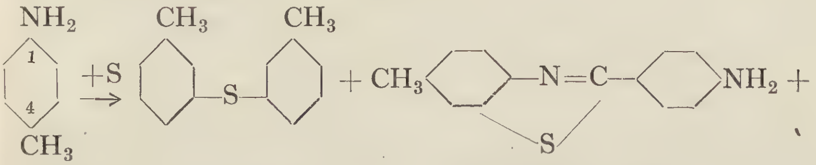
1:2:4-*Benzaldehyde disulphonic acid.*

8. SULPHUR MELTS

Primuline (*Green*),

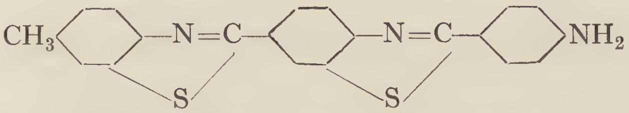
Chloramine Yellow FF (Naphthamine Yellow NN) and Thiazole Yellow, from *p*-Toluidine.

Generally speaking sulphur reacts with aromatic amines to give substitution products, two aromatic nuclei being joined together by a sulphur atom to give a thio-compound. A number of different bodies are, however, always produced simultaneously, and it is quite impossible to obtain homogeneous reaction products. Even by acting upon *p*-toluidine with sulphur four products are formed which may be easily recognized, in spite of various views which have been expressed to the contrary. These are in the first place unchanged *p*-toluidine, then thiotoluidine, dehydrothiotoluidine, and bis-dehydrothiotoluidine. The following formulæ indicate the constitution of the above substances :



p-*Toluidine*. *Thio*-p-*Toluidine*. *Dehydrothio*-p-*Toluidine*.

I. II.



“ Bis ”-dehydrothio-p-*Toluidine, or Primuline base.*

III.

214 Gms. (2 mols.) of *p*-toluidine are heated with 140 gms. *powdered* sulphur (*not* flowers of sulphur) and 2 gms. dehydrated sodium carbonate[1] to 180° in a stirring pot provided with a reflux condenser as shown on Plate XIV. (Fig. 36). Hydrogen sulphide is evolved which is absorbed either in caustic soda lye or by a tower filled with moist lumps of caustic soda.

214 gms.
p-Toluidine.
140 gms. S.
2 gms.
Na_2CO_3.

After about 8 hours the evolution of hydrogen sulphide slackens and the temperature is then raised slowly to 220°, and kept there for 5 hours. There is practically no further evolution of hydrogen sulphide, and the melt is then transferred to a flat tin tray where it solidifies to a light yellow crystalline cake. *Yield* 235 *gms.*

Separation of the Melt.

Method 1.—The cold, hard melt is finely powdered and intimately mixed with 1 % of its weight of dehydrated sodium carbonate, the purpose of which is to prevent the formation of lumps on sulphonation. 100 Gms. of the melt are added to 300 gms. monohydrate, the temperature being allowed to rise freely. As soon as all is in solution, which will occupy about an hour, the mixture is cooled to 25° with continuous stirring, and 200 gms. of 66 % oleum are allowed to drop in during an hour with good cooling and stirring, the

100 gms.
Malt.
1 gm.
Na_2CO_3.
100 gms.
100 %
H_2SO_4.
200 gms.
60 %
Oleum.

---

[1] The addition of soda is necessary in order to neutralize the traces of acidic substances which are always found in sulphur. If this is omitted, dark-coloured to black primuline melts are obtained almost invariably.

500 gms. Ice and 500 gms. H_2O.

About 50 gms. 20 % NH_3 + 800 gms. H_2O.

temperature being kept below 30°. After stirring for 5 hours at 30°, the temperature is raised to 40°, and kept there until a small test portion of the mixture dissolves readily in dilute ammonia. Complete solution is usually attained in 10 hours, but it is advisable not to stop the operation at this point as, for the subsequent filtration, the mass must be thoroughly sulphonated (cf. also sulphonation of β-naphthylamine on p. 37). The mixture is now poured on to 500 gms. ice and 500 c.cs. water, and filtered off after standing for 12 hours. The sulphonic acid is thoroughly washed out with cold water, by which means the greater part of the toluidine sulphonic acid and the thiotoluidine sulphonic acid is washed away. As soon as the washings show only a faint mineral acid reaction, the cakes are dissolved in about 50 gms. ammonia (20 % NH_3) and 800 c.cs. water, the whole being made up to 1200 c.cs. at 80°. The sparingly soluble ammonium salt of dehydro-thiotoluidine sulphonic acid separates out completely in the course of 2 days, when it is filtered and washed with a little 5 % ammonia. The mother-liquor contains the Primuline, which is precipitated at the boil with 15 % of common salt.

The yield of dry ammonium salt is about 25 *gms., and that of Primuline about* 80 *gms. of concentrated product.*

Method 2.—The finely powdered melt is extracted with alcohol of not less than 90 % strength. By this treatment the toluidine, thiotoluidine, and dehydrothiotoluidine go into solution whilst a pure Primuline base remains behind. The alcoholic extract is evaporated down to dryness, and the toluidine and part of the thiotoluidine are finally driven off by heating to 250°. The product so obtained is sulphonated with 25 % oleum.

Method 3.—The sulphonation is effected as before, and the washed sulphonic acid is dissolved at 80° in twenty times its volume of water and the necessary quantity of caustic soda lye, after which sufficient salt is added to give an 8 % solution, and the whole is filtered at 75°. The Primuline remains behind, whilst the dehydrothiotoluidine sulphonic acid is dissolved in the form of its easily soluble sodium salt, which may subsequently be salted out.

Primuline, discovered by A. G. Green, was the first artificial direct yellow dye which could be diazotized on the fibre and developed by means of phenols or amines to give dyeings fast to washing. On treatment with β-naphthol, Primuline Red is formed, which was at one time made use of to a very large extent. The fastness to washing is good, but the fastness to light is insufficient ; further, it cannot be discharged to a white, but only to a yellow, as the Primuline base withstands the action of all discharging agents.

Naphthamine Yellow NN (and FF) and Thiazole Yellow.

Originally dehydrothiotoluidine was a by-product, and in the early days of Primuline manufacture was melted up with sulphur to Primuline base. Nowadays this relationship has quite altered as the originally worthless dehydrothiotoluidine has now become the chief product. Unfortunately it is not possible so to conduct the melt that only the simple dehydrothiotoluidine is formed, and statements to the contrary are incorrect. At the present time Primuline is the by-product, and is sold for what it will fetch. The dyes which are manufactured from dehydrothiotoluidine are of various kinds. The free base or its sulphonic acid is diazotized and then combined with various naphthol sulphonic acids, *e.g.* with the so-called ε-acid (= naphthol disulphonic acid 1:3:8). This colour is distinguished by its great purity, and can be discharged completely to a pure white. Direct red dyes of this kind come into the market under various names and are referred to usually as dyes of the Erika Red type.[1] Besides the actual azo colours derived from dehydrothiotoluidine, two other products are prepared which are important yellow dyes. The first of these is *Naphthamine Yellow NN* or *Chloramine Yellow* (Kalle & Co.), formed by oxidizing dehydrothiotoluidine-sulphonic acid with sodium hypochloride, whilst the other is *Thiazole Yellow* or *Clayton Yellow*, which is produced by combining diazotized dehydrothiotoluidine-sulphonic acid with a second molecule of the same compound ; by this means a diazo-amino compound is formed which is further described below.

It may also be noted that by alkylating Primuline handsome yellow basic and acid dyes are formed which have not, however, any great importance.

Naphthamine Yellow NN.

Formula :

$$\left.\begin{array}{c}\text{Dehydrothiotoluidine-}\\ \text{sulphonic acid.}\end{array}\right\} -N=N- \left\{\begin{array}{c}\text{Dehydrothiotoluidine-}\\ \text{sulphonic acid.}\end{array}\right.$$

67·4 Gms. (2/10 mol.) of pure 100 % ammonium salt of molecular weight 337, corresponding to 14 gms. sodium nitrite, are dissolved in exactly 8·2 gms. 100 % caustic soda, and 300 c.cs. water, and the ammonia is then boiled off, as even traces of ammonia upset the oxidation. After an hour, when the odour of ammonia has

67·4 gms. 100 % NH_4 salt.
8·2 gms. NaOH.
About 300 c.cs. H_2O.

---

[1] Erika Z of the Berlin Aniline Co. is the combination : Dehydro-thioxylidine + ε-acid. Similar dyes are obtained from naphthol disulphonic acid 1:3:6.

10·5 gms.
100 %
HClO.

disappeared, the solution is made up to 500 c.cs. at 20°, and is mixed with 10·5 gms. HClO in the form of an approximately 5 % sodium hypochlorite solution. Both the ammonium salt and the hypochlorite must be exactly determined by titration. The temperature rises about 4° and after 1 hour a small test-portion is heated in a test-tube and salted out. The precipitate must be a pure orange, and potassium-iodide-starch-paper should show clearly the presence of hypochlorous acid. If this is not found to be the case a further quantity of hypochlorite is added. After standing for 5 hours, the mixture is boiled up, precipitated with 15 % of common salt, and the product filtered off. *Yield about 75 gms. strong dye.*

Naphthamine Yellow NN is the fastest to light of all yellow cotton dyes, and is completely stable towards chlorine. For this reason it is used in large quantities in the United States, where the washing is always treated with bleaching agents. It is not so pure as Chrysophenine, and is inferior to it as regards strength.

Thiazole Yellow or Clayton Yellow.

Formula :

$$\left.\begin{array}{c}\text{Dehydrothiotoluidine-}\\ \text{sulphonic acid.}\end{array}\right\} -N_2-NH- \left\{\begin{array}{c}\text{Dehydrothiotoluidine-}\\ \text{sulphonic acid.}\end{array}\right.$$

14 gms.
Nitrite
dehydro-thiotoluidine-sulphonic
acid.
25 gms.
50 %
NaOH.
25 c.cs.
30 %
HCl.
7 gms.
$NaNO_2$.
25 gms.
Na_2CO_3.
25 c.cs.
20 %
NH_3.

An amount of dehydrothiotoluidine-sulphonic acid corresponding to 14 gms. sodium nitrite are dissolved in 25 gms. 30 % caustic soda, and the solution is divided into two equal parts, one of which is acidified with 25 c.cs. concentrated hydrochloric acid. It is diazotized at 10° during 2 hours with 7 gms. of 100 % sodium nitrite. The orange-yellow diazo-compound is then run into the other half of the sulphonic acid, to which a further 25 gms. dehydrated sodium carbonate in a little water and 25 c.cs. strong ammonia have been added. The temperature during the coupling should be 4–5°, and it is advisable to keep the solution as concentrated as possible. After 2 hours the liquid is heated up to 30° and allowed to stand over-night. Next day it is heated up to 80° and salted out with 20 % of salt. *The yield of strong dye is about 85 gms.*

Thiazole Yellow (Clayton Yellow, Mimosa, etc.) is, in contrast to Chloramine Yellow, the most fugitive yellow in the whole dye industry, and it is a matter for surprise that such a product should ever have been used at all.

Thiazole Yellow is altered by caustic soda solution from a pure yellow to a bright red, for which reason it is used as a reagent for caustic alkali (see "*Thiazole paper*"). As already mentioned, it is extremely loose, but possesses great purity and strength, so that it is, unfortunately, used for dyeing cheap qualities of textile goods.

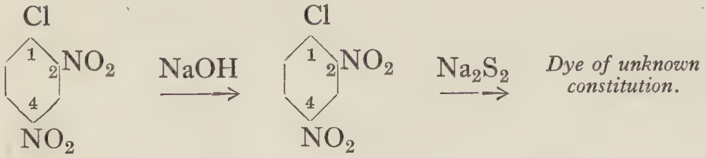
On sulphonating colour bases of the Primuline type by the "bake process," sulphonic acids are obtained which form azo colours faster to light than those prepared from the ordinary sulphonic acid. It is assumed that on "baking" the sulphonic group enters in the *o*-position to the amino group, by which means the fastness to light is considerably increased; attention has already been called to this relationship in connection with the pyrazolone colours.

Notes on Works Technique and Practice.—The preparation of the Primuline melt is carried out in pots heated in an oil-bath and provided with reflux condensers which are filled with hot water to prevent the *p*-toluidine which sublimes from stopping up the tubes. The hydrogen sulphide is collected in caustic soda solution and used for reductions. In the early days of the manufacture of Primuline the hydrogen sulphide was simply burnt under the boiler, which is a thoroughly irrational proceeding and distinctly unpleasant for the neighbourhood. The extraction with alcohol is carried out in iron boilers provided with perforated bottoms so that the alcohol may be constantly redistilled and used again as in a Soxhlet extraction apparatus. After distilling off the alcohol from the extract the residue is reheated in the oil-heated boiler to 240° until toluidine ceases to be evolved.

Analogous products to Chloramine Yellow, Thiazole Yellow, etc., may also be prepared from Primuline itself, but these colours are much redder, weaker, and duller in shade, so that they are little in demand.

Sulphur Black T from Dinitrochlorbenzene.

Reaction :



70 Gms. dinitrochlorbenzene are heated to 90° with stirring in a glass or iron vessel with 120 c.cs. of water, and to it is added during 2 hours 108 gms. of 35 % caustic soda solution, so that the reaction never becomes strongly alkaline. Heating is continued until a test portion dissolves to a clear solution in water, a further quantity of

120 c.cs. Water.
70 gms. Dinitrochlorbenzene
108 gms. 35 % NaOH.

50 gms. S.
125 gms. H_2O.
125 gms. cryst. Na_2S.

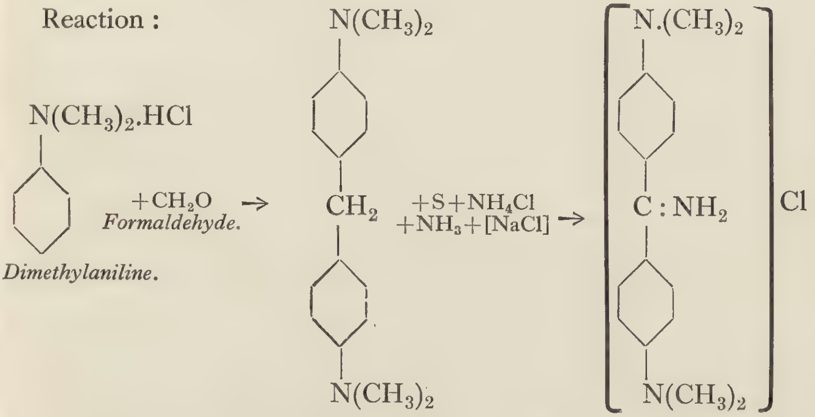
caustic lye being added if necessary. The suspension of the sodium salt of dinitrophenol is cooled to 45°, and to it is added a solution of 50 gms. sulphur and 125 gms. crystalline sodium sulphide in 125 gms. water. The temperature is then raised to 60°, the total volume being 600 c.cs. The mixture is next heated cautiously to 80° on the water-bath, and then, in the course of 2½ hours, to 105°, on an oil-bath. The mass is now boiled under a reflux for 30 hours without stirring, and is then diluted with 600 c.cs. water. After cooling down to 60° air is blown through the liquid until the dye is completely precipitated, when it is filtered off and dried at 70°. *The yield is about 70 gms.* Cotton is dyed at the boil, using four times the weight of crystalline sodium sulphide calculated on the weight of dye.

Notes on Works Technique and Practice.—Sulphur Black T is the most important Sulphur Black on the market, and is superior to other brands as regards fastness to washing and light. Charges of 500–1500 kilos. of dinitrochlorbenzene are made use of in the works, the melt-pots having capacities up to 12,000 litres and the oxidizing vessels up to 30,000 litres. With such large charges it is unnecessary to heat externally, as the heat of the reaction suffices. The pots are made of cast-iron, and are rapidly corroded. From the mother-liquor sodium thiosulphate may be obtained which is used in photography and in the textile industries ; a certain portion is also used in the dye-works for the production of Methylene Blue. The price of Sulphur Black T was formerly about 80–90 centimes per kilo. for a 35 % product, so that only those colour factories can make it successfully which are careful to use up all by-products. Further, those colour factories which do not manufacture chlorbenzene and dinitrobenzene are practically out of the running.

Auramine OO

(according to Traugott Sandmeyer).[1]

Reaction :



Dimethylaniline. *Tetramethyl-diamino-diphenylmethane.* *Auramine OO.*

(a) *Tetramethyl-diamino-diphenylmethane.*

242 Gms. of pure dimethyl aniline are mixed with 140 c.cs. of water and 260 gms. of hydrochloric acid (30 %), and to it is added at 30°, 60 gms. of 40 % formaldehyde, the strength of which has been accurately determined beforehand by titration. The ratio of formaldehyde to dimethylaniline is 1·1 : 2 molecules.

The mixture is heated up to 85°, with occasional stirring, for 5 hours, and the base precipitated with about 120 gms. of soda dissolved in a little water. The product is filtered off at 20° and is thoroughly washed with water. As the melting point is 90°, the drying temperature should not exceed 60°. *Yield about 255 gms., i.e.* practically quantitative.

242 gms. Pure dimethylaniline.
260 gms. 30% HCl.
140 gms. H_2O.
60 gms. 40 % CH_2O.
About 120 gms. Na_2CO_3.

(b) *Auramine OO.*

127 Gms. diamino base, 32 gms. sulphur, 70 gms. ammonium chloride, and 1000 gms. common salt are heated up to 110° in a stirring-pot similar to that shown on Plate XIV., Fig. 36. It is essential that all the substances should be finely divided and should contain no water. The temperature is raised to 130° during 2 hours,[2]

127 gms. base.
32 gms. S.
70 gms. NH_4Cl.
1000 gms. NaCl.

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[1] In the patent literature Auramine is connected with the meaningless name of *Feer*. The true discoverer was *Sandmeyer*, whose name was lost sight of owing to the heated controversy as to the ownership of the colour.

[2] Oil-bath about 25° higher.

$+NH_3$. a rapid stream of dry ammonia being passed into the apparatus from a cylinder. Any moisture is carried away by the gas, and at about 140° a vigorous evolution of hydrogen sulphide begins, which lasts from 5–7 hours, according to the speed of the stream of ammonia. The temperature is raised to 145° during 5 hours, the stirring being continued, and the hydrogen sulphide absorbed in concentrated caustic soda lye. It is also advisable to keep up a slight excess pressure of about 1/5 atms., measured by a manometer, by throttling down the exit tube. The speed of the ammonia stream should be about 5 bubbles per second. Before use the ammonia must be passed through a wash bottle containing 50 % potash, and then through two towers filled with lumps of caustic soda.[1]

When the evolution of hydrogen sulphide has ceased, the autoclave is opened and the brownish-yellow powdery mass is put into a large porcelain basin. 3 litres H_2O. The powder is covered with 3 litres of water to dissolve out the salt, after which the dye is filtered off and dissolved in 1½ litres of water at 60°. The temperature must not exceed this, as Auramine readily decomposes. The solution is filtered from the residue, consisting of a little sulphur and some Michler's ketone, and the filtrate is mixed with a litre of the salt solution previously obtained, the Auramine coming down in beautiful, glistening, golden leaflets. *The yield of pure dry colour may reach* 175 *gms.* It dyes cotton mordanted with tannin and tartar emetic a pure yellow.

Notes on Works Technique and Practice.—Auramine is the most important basic yellow dye, and is much valued owing to its extremely pure shade. The manufacture is carried out in oil-jacketed boilers which must be very accurately heated, as the slightest variation diminishes the yield. Use is also made of Frederking autoclaves, which can be very carefully regulated. Plate VIII., Fig. 24, shows such a flat Auramine pot with modern steam heating. The purity of the salt used has a very considerable influence ; traces of the chlorides of calcium or magnesium, which are present in all ordinary salt, have an injurious effect. The best salt is Galician rock-salt, which is almost chemically pure. The ammonia is dried in small towers filled with caustic soda. Only sufficient ammonia is added to give an excess pressure of half an atmosphere, and the gas is then circulated over the salt mixture by means of a pump. The hydrogen sulphide is absorbed and is used for reductions in the form of sodium sulphide. When the operation is properly conducted the yield may be up to 132 %, *i.e.* 132 kilos. of pure 100 % Auramine may be obtained from 100 kilos. of tetramethyl-diamino-diphenylmethane. It is difficult to estimate the yield as very few people are able to determine exactly the precise strength of dyeings on tannined cotton. For this reason it is usual to estimate this dye by titrating with titanous chloride of known strength until a weighed portion is rendered colourless, rather than by dyeing trials.

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[1] Ammonia cannot, of course, be dried with calcium chloride, as all amines combine with it.

In addition to Auramine OO, Auramine G is also prepared from monomethyl-*o*-toluidine ; it is purer and greener than the OO brand. The product from diethylaniline is not made as it comes out in such a resinous form on salting out that it is impossible to work it up.

Auramine is used on a very large scale for dyeing cotton, and more especially paper. The Swedish match factories alone use about eight waggon-loads a year for dyeing yellow match-boxes.

9. MISCELLANEOUS DYES

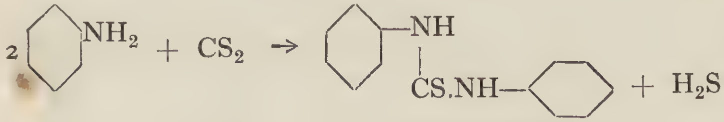
Indigo

(Traugott Sandmeyer's Method).[1]

Although Sandmeyer's Indigo synthesis is no longer worked, it affords such a classical example of the co-operation between science and technology that an account of it cannot be excluded from this book. This synthesis is one of the most remarkable achievements in the whole domain of dye chemistry, and may be compared with Leblanc's process for the manufacture of soda. Like the latter, it has exerted a fertilizing influence on the whole subject, and one portion of the process is still utilized for the production of isatin and its derivatives ; these relationships will be discussed later.

Before describing the individual operations, the chemical mechanism of the reactions must be examined.

(*a*) Aniline is converted into A. W. Hoffmann's "thiocarbanilide" by heating with carbon bisulphide :



Thiocarbanilide (m.p. 151°)
(A. W. Hoffmann),

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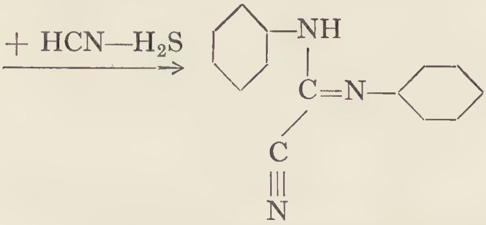
[1] See, also, Sandmeyer, *Zeitschrift für Farben- und Textil-Chemie*, 1903, **7**, 129 ; and *Helvetica Chimica Acta*, vol. ii., 234 (1919).

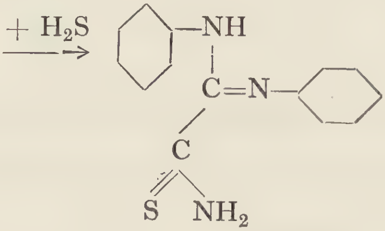
(*b*) The sulphur is removed from the Thiocarbanilide by means of basic lead carbonate, and at the same time hydrocyanic acid is added on, leading to the formation of Laubenheimer's "hydrocyancarbodiphenylimide":



M.p. 137°

Hydrocyancarbodiphenylimide (Laubenheimer).

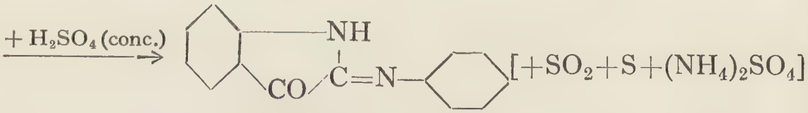
(*c*) The hydrocyancarbodiphenylimide is converted by means of yellow ammonium sulphide into the thio-oxamide-diphenylamidine, or more simply "thioamide":



M.p. 161–162°.

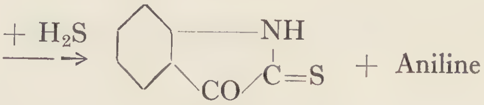
Thioamide.

(*d*) Under the influence of concentrated sulphuric acid the thioamide is converted readily into α-isatin-anilide:

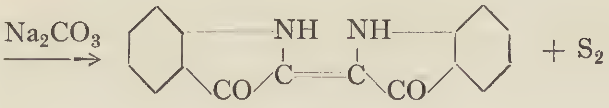


α-Isatin-anilide. M.p. 126°.

(*e*) The α-isatin-anilide may be converted into Indigo in various ways; it is either reduced in alcoholic solution with dilute ammonium sulphide, or it is converted into the α-thio-isatin, which yields Indigo at once with alkalis. The last method has been chosen here as this was the process formerly made use of in the industry:



α-Thio-isatin.



Indigo.

(a) *Thiocarbanilide.*

186 Gms. pure aniline are boiled up with 100 gms. of pure carbon bisulphide until the evolution of hydrogen sulphide ceases, which takes about 2 days. The temperature of the oil-bath is then raised to 160°, and the excess of bisulphide distilled off. The fused thiocarbanilide is poured on to a flat tray to cool, and is then powdered. It is sufficiently pure for further treatment, but may be obtained chemically pure by recrystallizing from three times its weight of alcohol. *The yield is about* 230 *gms.* M.p. 151°.

186 gms. Aniline.
100 gms. CS_2.

(b) *Hydrocyancarbodiphenylimide.*

350 Gms. lead nitrate, dissolved in a litre of hot water, are carefully precipitated at 95° with about 120 gms. dehydrated sodium carbonate and the precipitate is thoroughly washed with water. The moist basic lead carbonate is mixed with 600 gms. of 90 % alcohol in a 2-litre bolt-head provided with a stirrer and reflux condenser (Fig. 9), and is stirred up to a completely homogeneous paste; to it is then quickly added 228 gms. (1 mol.) of very finely powdered thiocarbanilide, and at 25° about 60 gms. of commercial sodium cyanide (=1·3 mol.).[1] The temperature of the mixture must be raised during an hour to 70° with vigorous stirring, and a small test-portion is then filtered off. The colourless solution should no longer blacken a pinch of basic lead carbonate. If this is not the case, heating must be continued for a further hour and the test again applied; if complete desulphurization has still not been effected a little more lead carbonate and sodium cyanide may be added, but if the correct amounts of the reagents have been taken no further addition will be necessary.

350 gms. $Pb(NO_3)_2$.
About 120 gms. Na_2CO_3.
600 gms. Alcohol.

228 gms. Thiocarbanilide.
60 gms. NaCN.

As soon as the sulphur reaction is no longer given the mixture is heated up to boiling, and the hot solution is filtered off. The residue is extracted twice more with half a litre of alcohol, and the hydrocyancarbodiphenylimide allowed to crystallize out. *The first fraction is quite pure, and weighs about* 160 *gms.* After evaporating down the mother-liquor, *a further* 40 *gms.* of practically pure product is obtained. *The yield is about* 98 %. The hydrocyancarbodiphenylimide crystallizes in fine yellowish prisms, having a melting point of 137°. The mother-liquors contain prussic acid, and must be handled with due care.

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[1] The HCN content of the sodium cyanide must be determined.

(c) "*Thioamide.*"

200 gms. Hydrocyancarbodiphenylimide.
35 gms. H_2S.
460 gms. 20 % NH_3.
25 gms. S.

The addition of hydrogen sulphide to the hydrocyancarbodiphenylimide takes place readily if it is very finely powdered, for which reason it is necessary to convert the product into the desired form either by grinding or by sifting. 200 Gms. hydrocyancarbodiphenylimide are emulsified with 500 gms. yellow ammonium sulphide solution at 35° by vigorous stirring. The ammonium sulphide solution is prepared by passing 35 gms. hydrogen sulphide into a suspension of 25 gms. powdered sulphur in 460 gms. of 20 % ammonia. If the hydrocyancarbodiphenylimide has been powdered sufficiently, the hydrogen sulphide adds on quantitatively within 12 hours, which may be recognized by the fact that a washed test-portion of the product dissolves in dilute hydrochloric acid. It is then filtered off and thoroughly washed with water ; the product is sufficiently pure for the next stage. *Yield about* 220 *gms.* It crystallizes from alcohol in yellow prisms having a melting point of 162°.

(d) *α-Isatin-anilide.*

The ring-formation giving isatin derivatives only occurs under certain very definite conditions ; it is important that hot sulphuric acid be used.

200 gms. Thioamide.
800 gms. 66° Bé. H_2SO_4.

200 Gms. of finely divided dry thioamide are added during a quarter of an hour to 800 gms. of 94 % sulphuric acid, at exactly 94° ; the mixture heats up fairly strongly and must be cooled. As soon as all has been added the mixture is heated for a further hour to 106–108°, after which time the evolution of SO_2 will have ceased. The solution is cooled down to 20° and is converted directly into the hydrochloride of α-isatin-anilide by pouring in a thin stream into a mixture of 1 litre water, 2 kilos. ice, and 500 gms. salt, stirring being continued without interruption. The hydrochloride of isatin-anilide separates out, mixed with finely divided sulphur, as a light reddish-brown precipitate.

1 litre H_2O.
1 kg. Ice.
500 gms. NaCl.

To obtain the anilide in a pure form it is filtered off and thoroughly washed with 20 % salt solution. The hydrochloride *freed from all acid* is then stirred up with water and dilute sodium carbonate solution

PLATE XIV.

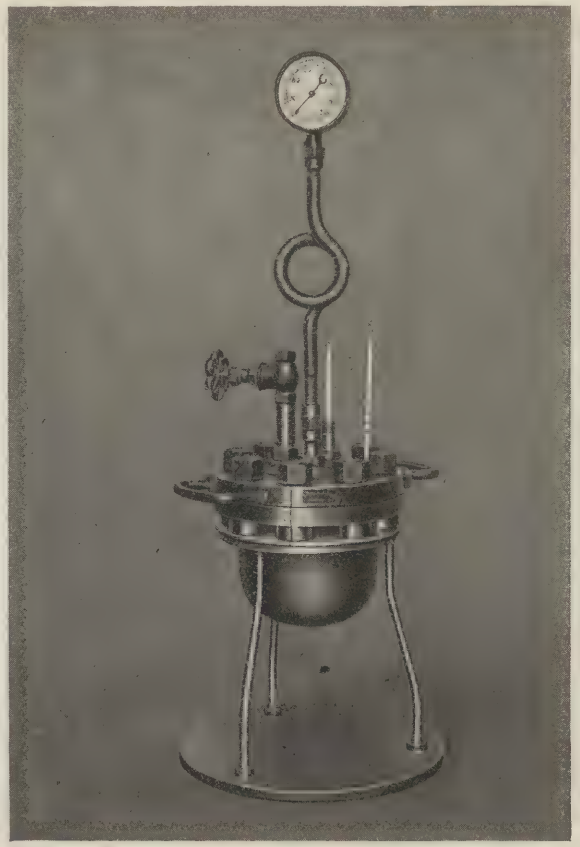


Fig. 35.—Cast-steel autoclave. Working pressure, 60 atms. Capacity, 1 litre. Weight, 30 kg.

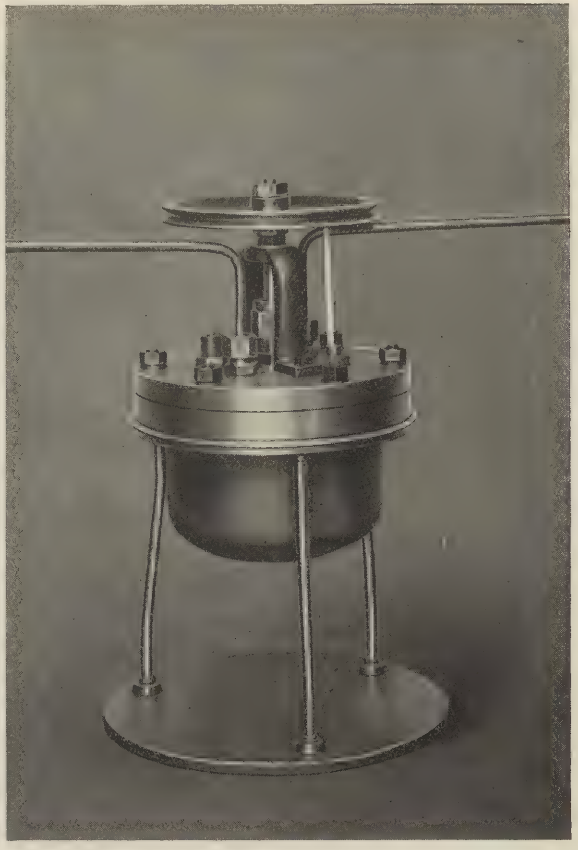
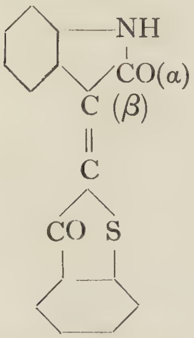


Fig. 36.—Cast-iron autoclave with stirrer. Working pressure, 1 atm. Weight, 12 kg. Copper oil-bath.

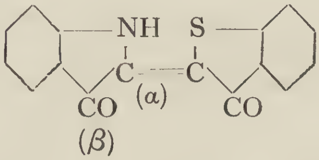
until there is a faintly alkaline reaction. The precipitate of anilide and sulphur is filtered off, thoroughly washed, and the dried mixture extracted with cold carbon bisulphide. Finally, the anilide is crystallized from hot alcohol, from which it is obtained in the form of dark needles having a melting point of 126°, *the yield from* 200 *gms. thioamide being about* 150 *gms. pure substance.* On boiling with a slight excess of dilute hydrochloric acid, the anilido group is split off as aniline, pure isatin being precipitated directly. M.p. 200–201°. It is recrystallized from hot water in which it is easily soluble. Isatin is an important intermediate for the synthesis of various valuable vat-colours. Of particular importance are those vat-dyes obtained from α-isatin-anilide by condensing with β-hydroxythionaphthene (Thioindoxyl). G. Engi was the first to notice that quite different dyes are obtained according to whether isatin itself be used or its anilide. Isatin condenses by exchanging the β-oxygen atom whilst the anilide, curiously enough, splits off the aniline and gives α-condensation products. The α-condensation products are much more valuable than the isomers.

From Isatin :



Thioindigo Scarlet R (Kalle).
Ciba Red G = Dibrom derivative.

From α-Isatin-anilide :



Ciba Violet B = Tribrom derivative.
Ciba Violet 3B = Dibrom derivative.
Ciba Grey G = Monobrom derivative.

(e) α-*Thioisatin and Indigo.*

In order to obtain Indigo from the solution of isatin-anilide in sulphuric acid it is not necessary to isolate either the pure anilide or the hydrochloride, but the thioisatin may be obtained directly from the solution. A solution of sodium hydrosulphide is prepared

45 gms. NaOH $+H_2S$.

by passing hydrogen sulphide into a solution of 45 gms. caustic soda dissolved in 150 c.cs. of water. This is then mixed with the sulphuric acid solution of isatin-α-anilide, from 200 gms. thioamide, by allowing both to run simultaneously into 6 litres of ice-water. A slight but distinct excess of sulphuretted hydrogen should always be present. The reduction occupies about half an hour, and the thioisatin separates out as a voluminous brown precipitate, aniline sulphate remaining behind in the solution. The thioisatin is filtered off as soon as a filtered test-portion of the liquid gives no further precipitate on treatment with sodium sulphide, which will be the case after about an hour. The precipitate is then washed until the mother-liquor has a specific gravity of only 1·007 (1° Bé). The washed precipitate is stirred up with 3 litres of water to which concentrated sodium carbonate solution is added until the reaction becomes strongly alkaline, about 30 gms. soda being required for this purpose. The formation of Indigo takes place very rapidly, and the mixture is preferably warmed for one hour at 60°, and is then left stirring over-night. Next day the Indigo and sulphur are filtered off, thoroughly washed, and dried at 80°. The dried colouring matter is then extracted with twice its weight of carbon disulphide, 80 *gms. pure Indigo being obtained.*

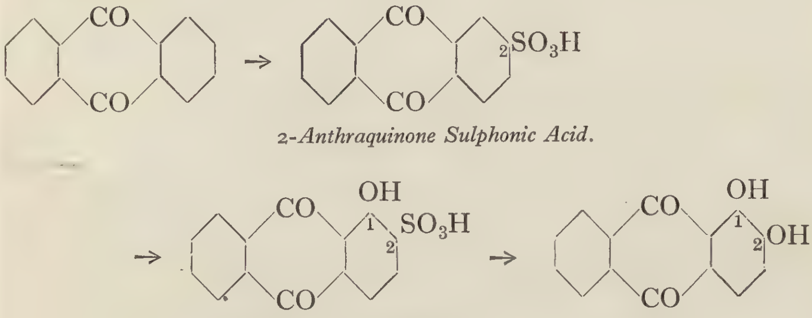
6 litres Ice + water.

About 30 gms. Na_2CO_3.

Notes on Works Technique and Practice.—The reactions involved in the Sandmeyer synthesis go surprisingly smoothly, the yield of dye calculated upon the aniline taken being about 80 % of that theoretically possible. The process was used for a short time by J. R. Geigy, the cost of production being 10·8 francs per kilogram of 100 % product. Indigo prepared by the Sandmeyer method vats better than any other artificial product, and was immediately welcomed by dyers. It was found to be possible to effect the entire manufacture without the use of a drop of alcohol, since all the substances involved react readily in aqueous solution if sufficiently finely divided. The chief difficulty is not the hydrocyanic acid, but the hydrogen sulphide, which is a dangerous industrial poison, as, after a short time, it can no longer be smelt. The lead sulphide may be split up by means of concentrated hydrochloric acid into lead chloride and hydrogen sulphide, the latter being returned to the process. Soon after the introduction of this promising method of manufacture it was displaced by the process of the Deutsche Gold-und-Silber-scheide Anstalt, as in this latter method the yields were also increased to about 85 % by the latest improvements so that effective competition was no longer possible. At the same time it is always conceivable that under favourable conditions the Sandmeyer process may again become of importance. Since the discovery by Frasch of the great sulphur deposits in Louisiana and the electro-thermal preparation of sodium cyanide and carbon disulphide this possibility must always be borne in mind.

Alizarin from Pure Anthraquinone.

Reaction :



2-*Anthraquinone Sulphonic Acid.*

1:2-*Hydroxyanthraquinone Sulphonic Acid.*

Alizarin.

(a) 2-*Anthraquinone Monosulphonic Acid Sodium Salt* (*Silver Salt*).

On treating anthraquinone with fuming sulphuric acid two sulphonic groups readily enter the nucleus so that it is necessary to reduce the quantity of SO_3 to such an extent that a fairly large portion of the anthraquinone remains unchanged.

100 Gms. of dry finely divided anthraquinone are added cautiously to 150 gms. of oleum containing 25 gms. of SO_3. The temperature must not exceed 30°, and stirring must be continued without interruption in order to prevent any local overheating. The temperature is raised during 4 hours to 120° by means of an oil-bath, and after a further 2 hours to 140°. The vessel must be kept well closed to prevent SO_3 from distilling off (see Fig. 4). After cooling, the mixture is poured into 3 litres of water and the unchanged anthraquinone filtered off. Some 25–40 gms. are recovered, according to the manner in which the sulphonation has been effected. The sulphuric acid solution is now completely neutralized by means of chalk or limestone as described on p. 15, and the calcium sulphate filtered off. The lime is then precipitated with dilute sodium carbonate until a filtered test-portion gives no further precipitate

100 gms. Anthraquinone.
150 gms. 25 % Oleum.

About 180 gms. $CaCO_3$.

with soda. The filtered solution is evaporated down to 400 c.cs. over a gas-ring, and is then allowed to cool. The sodium salt of the anthraquinone-2-sulphonic acid separates out in the course of a couple of days as a glistening, silvery precipitate. It is filtered off and washed with a little water. *The yield of dry substance is* 60–90 gms. A few grams of less pure substance may be recovered from the mother-liquor, but always contain a little disulphonic acid, no matter how carefully the sulphonation is carried out.

It is also possible to avoid liming-out, as is usually done technically, by pouring the sulphonation product into a litre of water, filtering from unchanged anthraquinone after standing for an hour, and then salting out with 20 % of common salt. The precipitated sodium salt is filtered off, washed with a little concentrated brine, and pressed. It is then pure enough for the melt. With proper working the mother-liquors contain only 2–2½ % of disulphonic acids, which may be rejected. In the works rather more concentrated oleum is used, about 40 %, as in this case there is less danger of over-sulphonating.

(b) *The Alizarin Melt.*

The alizarin melt was first introduced into chemical technology by Caro, and the addition of an oxidizing agent, saltpetre, was first made use of by the Society of Chemical Industry in Basle. At the beginning of the 'seventies chlorates were made use of, following the suggestion of Koch, and at the present day only the cheap electrolytic sodium chlorate is utilized.

100 gms. Silver salt. (100 %). 260 gms. NaOH. 28 gms. $NaClO_3$.

100 Gms. of 100 % silver salt are heated with 260 gms. 100 % caustic soda, 28 gms. sodium chlorate, and sufficient water to make the total volume up to 670 c.cs., the mixture being heated up with continuous stirring in an autoclave to 185°, the pressure attaining 5–6 atmospheres. After 48 hours the melt is allowed to cool, and is then examined to see if it is finished. For this purpose 2 c.cs. of the melt are taken, the Alizarin precipitated with the requisite quantity of concentrated hydrochloric acid, and the filtrate extracted twice with a little ether. The liquid, from which all Alizarin has been removed, is now diluted to 15 c.c., and the fluorescence observed, which is due to unchanged silver salt or to monohydroxyanthraquinone sulphonic acid. Only a very faint fluorescence should be observable, or none at all, and if necessary the melt is heated up again to 190° for 24 hours. The product is then diluted with 2 litres of water and the Alizarin precipitated *at the boil* with 50 %

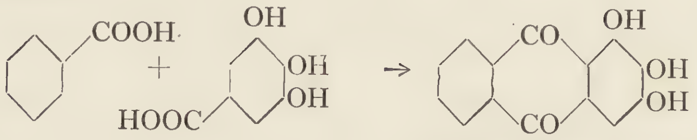
sulphuric acid ; after filtering off at 50° it is washed until the mother-liquor is free from salt. The Alizarin is not dried, as when once dry it no longer dyes properly. The yield is estimated by determining the moisture and by test-dyeings. Usually the finished product contains 20 % of colouring matter.

About 70 gms. pure Alizarin are obtained from 100 gms. of pure silver salt.

Notes on Works Technique and Practice.—Next to Indigo, Alizarin is the most important product produced by the colour factories. Owing to its low price it is now made only at a few works, but on a very large scale. The sulphonation is effected in apparatus of the usual type, but the melts are being carried out more and more frequently in Frederking apparatus such as was shown on Plate VIII. (Fig. 23). As the chlorate melt attacks the apparatus very vigorously, a liner of alkali-resistant cast-iron is always used, which may be replaced. There are many different forms of such apparatus. On the works scale very large charges are used, so that as much as 2000–2500 kilos. 100 % Alizarin may be obtained at one operation in one pot ; the dye is then made up to 16 % or 20 % paste, the standardizing being done by determining the moisture content, and by dye-trials. Again it is possible technically to work with much less caustic soda, only 110 % of the theoretical quantity being required, corresponding to 40 gms. instead of 260 gms. in the present case. Alizarin which has been dried may be reconverted into a form suitable for dyeing by dissolving in borax and reprecipitating with acetic acid or sulphuric acid. Dyes of the alizarin type must, owing to their sparing solubility, be precipitated at the boil, as only in this manner can they be obtained in a suitably fine state of subdivision (cf. also Anthracene Brown). The world's production of 100 % Alizarin was about 2,800,000 kilos., of which the Badische Anilin and Soda Fabrik alone produced 2,000,000 kilos. For the Oriental market a solid preparation is made by adding sufficient starch to the dye to convert it into dry lumps which swell up to a paste on boiling with water, and dye easily. (For dyeing with Alizarin, see the pattern cards issued by the various firms, and Gnehm's " Taschenbuch.")

Anthracene Brown FF from Benzoic Acid and Gallic Acid.

Reaction :



1:2:3-*Trihydroxyanthraquinone, Anthracene Brown or Anthragallol.*

36·6 gms. Benzoic acid.
300 gms. 100 % H_2SO_4.
50 gms. Gallic acid.

36·6 Gms. (3/10 mol.) pure benzoic acid are dissolved in 300 gms. sulphuric monohydrate contained in a glass, porcelain, or iron beaker, and stirred until complete solution is effected. It is then heated up slowly to 90°, at which temperature 50 gms. pure dry gallic acid (dried at 110°) are added in small portions during an hour. The temperature is kept at 118° for 6 hours, and then the melt is allowed to drop very cautiously into a litre of boiling water with continuous stirring. The product is filtered off from the absolutely boiling liquid into a previously warmed jar, and the dye is well washed with hot water. The excess of benzoic acid crystallizes out in a pure form in a short time from the mother-liquor. After stirring up with water to 20 % paste the dye is ready for use. The dyeing is effected upon chrome-mordanted wool, chromium fluoride giving the handsomest and fullest shades.

Notes on Works Practice.—The most important factor in this manufacture is the absolute purity of the gallic acid used. No "second-quality" crystals may be used as these probably contain homologues of gallic acid which cause troublesome foaming during the condensation, and diminish the yield to 50 %. On the works also the boiling liquids are filtered through filter-presses made of pitch-pine and provided with nitro-filters. These latter will last out about 50 operations, but must of course be very carefully manufactured if they are to meet these exacting demands.

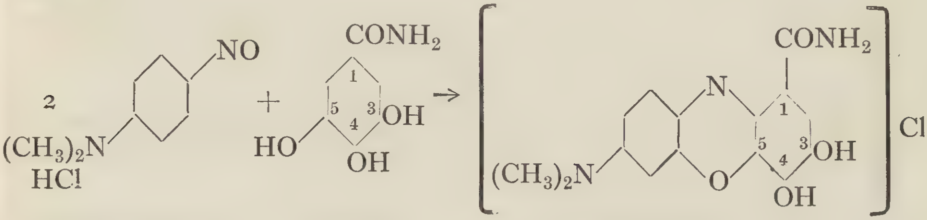
For the production of Anthracene Brown for printing (F. D.=für Druck) the process is very similar. The condensation, however, is carried out at 130–140° instead of at 118°. The product obtained by precipitating in boiling water is not sufficiently finely divided, but gives a mottled effect on printing. It is therefore necessary, after washing, to convert the product, as a 10 % suspension, into the sodium salt by means of soda at 80–90°, and then to precipitate cautiously with hydrochloric acid. After filtering off again, the product is made up to the desired strength in a Werner and Pfleiderer mixer. What was said before as to the purity of the gallic acid applies still more forcibly in the present case.

A good quality gallic acid may be easily prepared by hydrolysing tannin at 70° in concentrated solution with caustic soda lye of at least 40 %.[1] In order to protect the gallic acid from oxidation a little sodium bisulphite is added. The gallic acid is precipitated with concentrated hydrochloric acid (sulphuric acid must not be used), and is then crystallized from boiling water.

Gallamine Blue from Gallamide.

By heating nitroso-dialkylamines with gallic acid or its amide, well-defined compounds are obtained which are termed Oxazines. The gallic acid is obtained exclusively from natural tannin.

Reaction : [2]



p-Nitrosodimethylaniline. *Gallamide.* *Gallamine Blue* (R. Geigy).

(a) *Nitroso-dimethylaniline.*

100 Gms. dimethylaniline are mixed with 200 gms. 30 % hydrochloric acid and, after cooling, 300 gms. of ice are added. A concentrated solution of 60 gms. of 100 % sodium nitrite are then dropped in during 5 hours, the beaker being placed in ice-water. It is not possible to test for free nitrous acid with nitrite paper, as nitroso-dimethylaniline hydrochloride itself reacts with it. The excess, therefore, can only be recognized by its odour. The reaction to Congo paper should, of course, be shown the whole time. After standing for 6 hours, the product is filtered off, rinsed out into the filter by means of the mother-liquor, and the precipitate sucked as dry as possible. Finally, it is squeezed in a screw-press, and the moist nitroso-dimethylaniline powdered as much as possible. The salt

100 gms. Dimethylaniline.
200 gms. HCl.
300 gms. Ice.
60 gms. 100 % $NaNO_2$

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[1] The caustic lye must be free from chlorate so that electrolytic caustic cannot be used or else oxidation occurs on hydrolysis and acidification.

[2] One molecule of nitroso-dimethylaniline is used up as the oxidizing agent.

must not be dried, but is used in the fresh moist condition. On the large scale it is obtained in a sufficiently dry condition merely by centrifuging.

Para-nitroso-diethylaniline is obtained in a similar manner, except that, owing to the very great solubility of the hydrochloride, no water is used for the nitrosation but only concentrated hydrochloric acid and saturated sodium nitrite solution, with external cooling. In the works the process is carried out in enamelled vessels, as in the case of the Tropæoline coupling.

(b) *Gallamine Blue.*

20 gms. Gallamide.
500 gms. Alcohol.
Nitroso-dimethylaniline from 75 gms. dimethylaniline.

20 Gms. gallamide of 92 % purity [1] are dissolved in 500 c.cs. of 90 % alcohol contained in a glass bolthead provided with reflux condenser and stirrer (see Figs. 9 and 18A), and nitroso-dimethylaniline obtained from 75 gms. dimethylaniline are added in three portions to the boiling mixture. Preferably the additions are made at intervals of 15 minutes, so that the mixture is completed in three-quarters of an hour. The product is boiled up under reflux for a further 4 hours, and is then allowed to stand for 12 hours. The Gallamine Blue is obtained as a brilliant, glistening, bronzed precipitate which is filtered off and washed with water. The alcohol is redistilled. *The yield of pure Gallamine Blue is about* 40 *gms.* A grey dye similar to Nigrosine is obtained from the alcoholic mother-liquor, which gives fast grey shades with chrome acetate on cotton under the name of *Methylene Grey.*

Gallamine Blue is practically insoluble in water and can therefore not be used in this form. By means of various reactions, however, it may be converted into an easily soluble form.

1 part Gallamine Blue.
6 parts 25 % Bisulphite.

One part Gallamine Blue is warmed up to 50° on the water-bath with six parts of sodium bisulphite solution containing 25 % SO_2, until the evolution of sulphurous acid has ceased. If this is the case, after about an hour the product is heated up to 85° for 1–3 days until the colour of the mixture has become pure greyish-green. The dye obtained is a sulphonic acid of the leuco-compound (or possibly a complex sulphonic salt), and dyes wool, mordanted with chrome acetate, a beautiful and fast navy blue. It may also be used for printing cotton, but is overshadowed in importance by another colouring matter belonging to this group, namely, the *Modern Violet* of Durand and Hugenin, which is obtained as a leuco-compound by the reduction of Gallamine Blue with hydrogen sulphide, and affords extremely pure and fast chrome lakes on cotton :

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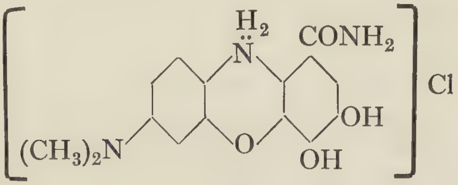
[1] The purity is determined by distilling off the ammonia with caustic soda solution and titrating.



Modern Violet (Durand and Hugenin).

50 Gms. Gallamine Blue are dissolved in about 40 gms. of 30 % caustic soda solution and 400 c.cs. water, and to the clear solution are added 50 gms. crystallized sodium sulphide. The liquid is acidified at 60° during one hour with about 100 gms. strong hydrochloric acid until a permanent reaction is given with Congo paper. The blue colour will have disappeared by this time, leaving a practically colourless solution, which is filtered from the precipitated sulphur, and the hydrochloride of the leuco compound salted out with 150 gms. common salt. It is then filtered off, washed with a little saturated salt solution, and well pressed out. The dye is dried in vacuo at 60° as it rapidly reoxidizes. *Yield about* 55 *gms.*

50 gms. Gallamine Blue.
40 gms. 30 % NaOH.
400 c.cs. H_2O.
50 gms. Na_2S+Aq.
About 100 gms. conc. HCl.
150 gms. NaCl.

Notes on Works Technique and Practice.—The oxazines are printing colours *par excellence.* In addition to the dimethylaniline derivatives the corresponding diethyl derivatives are also prepared, which are characterized by their very pure greenish shades (*Celestine Blue*). If gallic acid be used in place of gallamide, the *Gallocyanines* are produced which were accidentally discovered by Horace Köchlin ; he attempted to fix nitroso-dimethylaniline on cotton by means of tannin and tartar emetic, and so obtained blue colours which he recognized to be oxazines. The Gallocyanines cannot be manufactured conveniently in ethyl alcoholic solution, methyl alcohol being used instead, which is, however, less pleasant to work with owing to its poisonous nature and its volatility. Besides the simple oxazines there are also a number of more complex condensation products known, but we cannot enter into these here.

We may recall the fact that the first oxazine to attain to technical importance was *Meldola's Blue*, *Naphthol Blue*, or *Bengal Blue*, which is obtained from nitroso-dimethylaniline hydrochloride and β-naphthol. It is very fast, but does not give beautiful shades, and its dust attacks the mucous membranes so strongly that many people cannot work with it. In spite of this, however, it is still fairly widely used.

The large-scale plant is constructed of enamelled cast-iron with a reflux condenser made from lead tubing. A charge of 40 kilos. gallamide is used, the operation lasting about 12 hours.

Owing to its oxidizability Modern Violet must be ground up in the cold as otherwise spontaneous combustion may occur. The presence of finely divided sulphur is obviously the cause of this undesirable phenomenon.

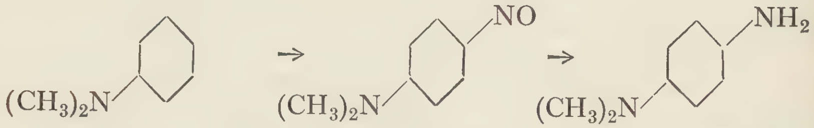
Methylene Blue from Dimethylaniline.

The formation of Methylene Blue is of interest both from the scientific and technical standpoints, and will therefore be discussed before the actual methods of preparation are described.

Nitroso-dimethylaniline is prepared from dimethylaniline by treating the latter with sodium nitrite in hydrochloric acid solution. This nitroso compound is reduced, giving *p*-amino-dimethylaniline.

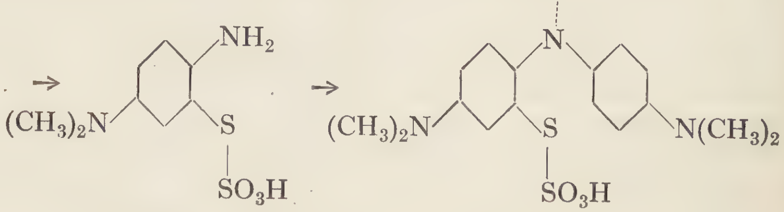
Reactions :

(*a*) *p*-Amino-dimethylaniline :



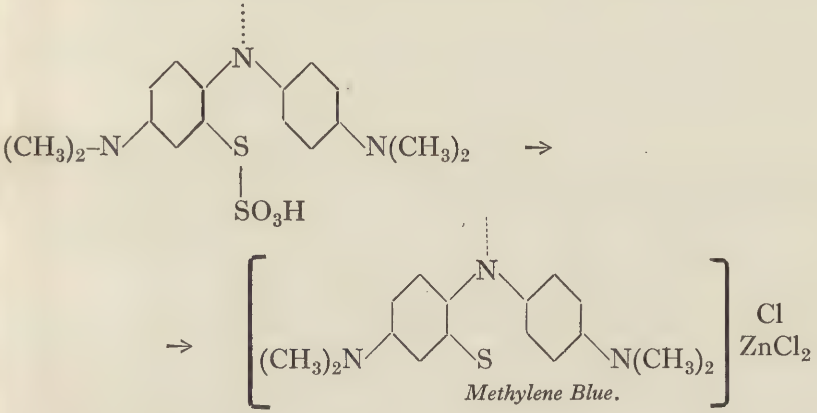
Dimethylaniline. p-*Nitroso-dimethylaniline.* p-*Amino-dimethylaniline.*

(*b*) The *p*-amino-dimethylaniline is oxidized in acid solution with a second molecule of dimethylaniline, and at the same time the thiosulphonic acid group is introduced into the molecule, which is effected by carrying out the oxidation in the presence of nascent thiosulphuric acid.



Thiosulphonic acid of p-*amino-dimethylaniline.* *Thiosulphonic acid of Bindschedler's Green.*

(*c*) The thiosulphonic acid is now converted into Methylene Blue by closing the ring with the aid of more oxidizing agent :



Methylene Blue.

(a) p-*Amino-dimethylaniline.*

24·2 Gms. (2/10 mol.) of pure dimethylaniline are dissolved in 75 gms. concentrated hydrochloric acid (30 %) and is then allowed to cool. The solution is treated with 150 gms. ice, and during 1 hour 14·7 gms. of 100 % sodium nitrite are run in as a 20 % solution, the nitrosation being complete in 4 hours. A further 110 gms. of 30 % hydrochloric acid are now added, together with 200 gms. ice, and 35 gms. good quality zinc dust are added during a quarter of an hour with mechanical stirring. The temperature may without danger be allowed to reach 25°. The solution is now colourless and neutral to Congo, and is filtered, the zinc dust being washed out with a very little water.

24·2 gms. Dimethylaniline.
75 gms. 30 % HCl.
150 gms. Ice.
14·7 gms. 100 % NaNO$_2$.
110 gms. 30 % HCl.
35 gms. Zinc dust.

(b) *Thiosulphonic Acid of Bindschedler's Green.*

The oxidation at this stage must be effected in the presence of a zinc chloride solution which has no reducing action. Such a solution may be prepared by dissolving sheet-zinc in concentrated hydrochloric acid.[1] The thiosulphuric acid is used in the form of aluminium thiosulphate, which is so strongly dissociated that it behaves like free thiosulphuric acid.

Before beginning the actual preparation of the Methylene Blue, solutions must be prepared of the necessary reagents, as an essential point in this operation is that the substances shall be added quickly and at the right temperature.

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[1] A method adopted in the works is to treat commercial zinc chloride liquor with sodium bichromate until there is no further reducing action ; frequently 100–250 gms. bichromate are required for 100 kilos. of zinc solution.

Solution I = 38 gms. pure aluminium sulphate in 60 c.cs. water.

Solution II = 52·5 gms. crystallized sodium thiosulphate in 50 c.cs. water.

Solution III = 57 gms. sodium bichromate made up to 90 c.cs.

Solution IV = 20 gms. dimethylaniline in 27 gms. strong hydrochloric acid.

"Solution" V = 25 gms. very finely powdered pyrolusite (MnO_2) made up into a homogeneous paste with 30 c.cs. water.

4 gms. 100 % H_2SO_4.
100 gms. 50 % $ZnCl_2$.
38 gms. $Al_2(SO_4)_3 + 18H_2O$.
52·5 gms. $Na_2S_2O_3 + 5H_2O$.
19 gms. $Na_2Cr_2O_7$.
38 gms. $Na_2Cr_2O_7$.
25 gms. MnO_2 (about 88 %).

The clear neutral solution of *p*-amino-dimethylaniline is made mineral-acid with 4 gms. concentrated sulphuric acid and 100 gms. of 50 % non-reducing zinc chloride solution is added. The beaker is placed on a felt pad and heated up by blowing in steam. Solution I is added at the ordinary temperature with good stirring, then Solution II, and after 2 seconds one-third of Solution III, corresponding to 19 gms. of sodium bichromate. By passing in dry steam the temperature is raised to 40° in one minute, Solution IV is added, then the remainder of Solution III, and the whole heated rapidly to 70°. The liquid becomes dark greenish-blue, owing to the formation of the thiosulphonic acid of Bindschedler's Green. As soon as 70° is attained, suspension V is added, and the whole heated to 85°.

The reason for adding the manganese dioxide is to convert the sulphurous acid which is set free during the ring-formation into the harmless dithionate. In place of the pyrolusite, 40 gms. copper sulphate may be used with equal success, the cupric salt being converted into the insoluble cuprous salt.

70 gms. H_2SO_4, 66° Bé.
1 litre H_2O.
50 gms. $ZnCl_2$, 50 %.
150 gms. NaCl.

At 85° the solution develops a fine bronzed appearance and the resultant dye is precipitated from the concentrated zinc chloride solution. After half an hour the mixture is allowed to cool to 50°, and 70 gms. concentrated sulphuric acid are added, which dissolves up the manganese salt, aluminium hydroxide, and chromic oxide. The product is filtered off at 20° and washed with a little 10 % brine. The crude blue is dissolved in a litre of water at 100°, filtered from insoluble matter, and the clear filtrate salted out with 50 gms. of ordinary 50 % zinc chloride solution and 150 gms. common salt. After 24 hours, the zinc chloride double salt comes out as a fine red bronzed precipitate which is filtered off and washed with a little 10 % salt solution; it is then dried at a temperature not exceeding 50°, *a yield being obtained of about* 44 *gms. pure concentrated colour.*

Notes on Works Technique and Practice.—The method described above was originated by Bernthsen and Ulrich, who also recommended the use of aluminium thiosulphate. The use of pyrolusite or copper sulphate is general. Large quantities are not dealt with at one time as quick heating up is essential. On the large scale the finished dye is usually filtered off in frame-filters (see Plate VI.), and after draining, is put into small bags and centrifuged.

Owing to its very pure shade and low price, Methylene Blue is highly valued, and is much used for dyeing tannined cotton. For silk printing the *zinc-free Methylene Blue* is used for the production of discharge effects. The zinc-free product is obtained by dissolving ordinary Methylene Blue in water, precipitating the zinc with sodium carbonate, and filtering off the solution of the easily soluble Methylene Blue base. By the addition of hydrochloric acid and common salt, the zinc-free Methylene Blue is precipitated out in fine crystals. On the large scale the crystallization occupies several days, and is assisted by cooling with lead pipes through which cold water is circulated.

Of equal importance with the zinc-free salt of Methylene Blue is the nitro compound which is known as *Methylene Green.* The nitration is effected in a similar manner to that of Tropæoline, and the crude zinc chloride double salt may be nitrated directly.

The crude, moist, Methylene Blue as obtained above is made into a paste with 50 c.cs. water and 20 gms. of 60 % nitric acid (40° Bé.), and to it is added at 25°, 5 gms. sodium nitrite dissolved in the minimum quantity of water. The temperature is then raised cautiously to 50° with good stirring and kept there for 2 hours.

The product is diluted up with 200 gms. of saturated brine, and the precipitate filtered off after 12 hours. The crude product is dissolved in 1 litre of water at a temperature not higher than 60°, the solution filtered and the dye precipitated by means of 150 gms. salt and 50 gms. of 50 % zinc chloride solution. After standing for 12 hours the colour is filtered off and dried at 45° until it can be powdered. It still contains about 20 % of water. If it is dried completely its strength is quickly diminished, a portion becoming insoluble. *The yield from the above quantities is about 37 gms. of concentrated product.*

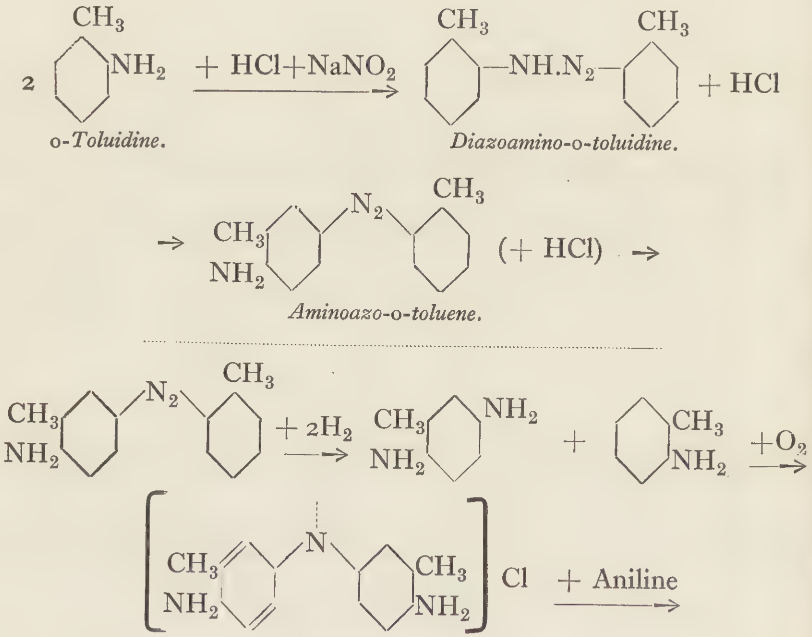
Crude Blue (2/10 mol.).
50 c.cs. H_2O.
20 gms. HNO_3.
5 gms. $NaNO_3$ (approx. 93 %).
200 gms. NaCl soln.
1 litre H_2O.
150 gms. NaCl.
50 gms. $ZnCl_2$ (50 %).

Methylene Blue and Methylene Green are brought down to standard with dextrine, as the addition of salt diminishes the solubility too much. The most important use for Methylene Green is in combination with iron-mordanted logwood for dyeing blacks on silk, but it is also much used in conjunction with tin phosphate.

The black dyeings obtained in this manner are amongst the finest and fastest blacks for silk.

If diethylaniline or dimethyl-*o*-toluidine are used in place of dimethylaniline, the pure greenish *Thiazine Blue*, also known as *Thionine Blue*, etc., is obtained, which serves for the production of pure blue shades on silk; its importance, however, is decreasing owing to the competition of the faster Alizarin colours. The non-alkylated Methylene Blue, diamino-phenazthionium chloride or *Lauth's Violet*, is used to a very limited extent for pure violet shades. It is still made by the old method, which consists in oxidizing aniline, *p*-phenylene diamine, and hydrogen sulphide with ferric chloride.

Safranine from *o*-Toluidine and Aniline.[1]


CH3
2
NH2
+ HCl+NaNO2
CH3
—NH.N2—
CH3
+ HCl
o-Toluidine.
Diazoamino-o-toluidine.
CH3
N2
CH3
NH2
(+ HCl)
Aminoazo-o-toluene.
CH3
N2
CH3
NH2
+ 2H2
CH3
NH2
NH2
+
CH3
NH2
+O2
N
CH3
NH2
CH3
NH2
Cl
+ Aniline

o-Tolyl-indamine.

The methods of formation of the Azines, and of Safranine in particular, are very closely connected with those of the Thiazines (see p. 174). Of the numerous methods given in scientific literature there is only one of practical importance,[2] namely, that in which

[1] For more exact details, see J. Walther, "Aus der Praxis der Anilinfarbenfabrikation," pp. 21 *et seq.*; 291 *et seq.*

[2] With the exception of the Anthraquinone-azines, and certain dyes of less importance.

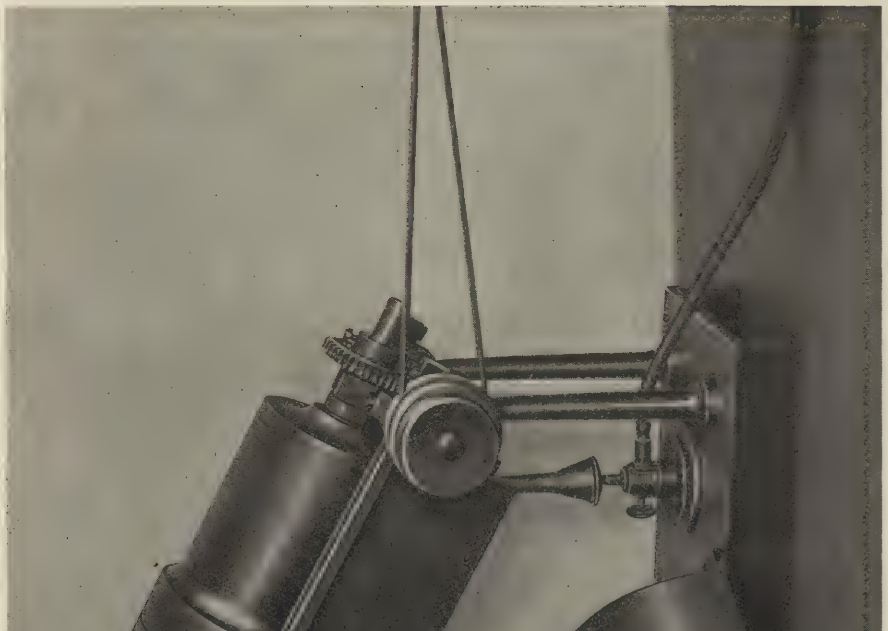
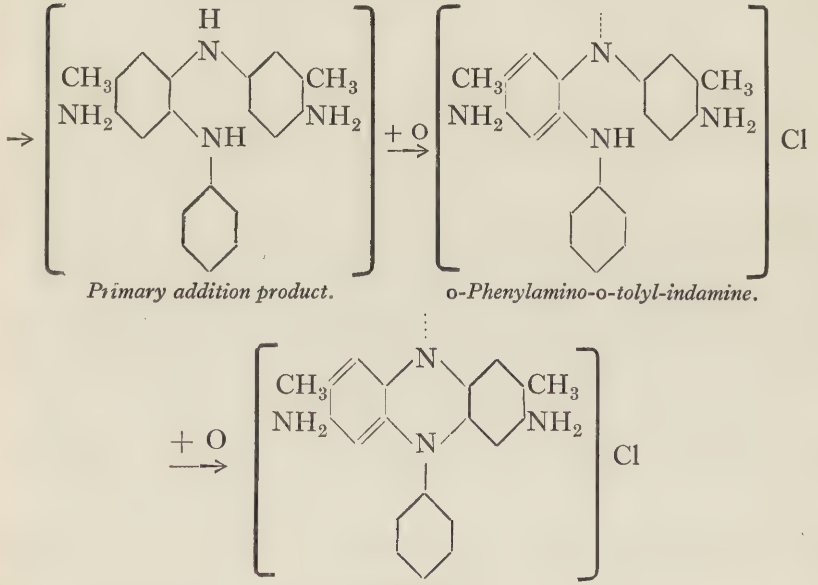


FIG. 37.—Wrought-iron rotating autoclave with worm-drive. Weight, 11 kg. Capacity, 400 c.cs. Working pressure, 100 atms.

(as in the case of Methylene Blue), a para-diamine is oxidized with a mono-amine to give the Indamine, from which the actual azine dye is produced by the closing of the ring. In the case of Methylene Blue the thiazine ring is closed with a sulphur atom, derived from the thiosulphonic acid, whilst in the case of Safranine this position is taken up by an aromatic mono-amine, usually aniline. The mechanism of the reaction is indicated in the above scheme.

Instead of isolating the pure aminoazo-toluene, the resultant azo compound may be reduced straight away. By this means one molecule of *p*-diamine is formed together with two molecules of a monoamine.[1] Many chemists prefer, however, to separate out the aminoazo-*o*-toluene first, which is then reduced, and the mixture of *p*-diamine with the mono-amine is oxidized to the Indamine.

On oxidizing this Indamine together with hydrogen sulphide, for example by means of ferric chloride, the homologue of Lauth's Violet is produced. As a so-called quinoid Indamine it is able to condense with a variety of substances. With aniline, under the oxidizing influence of chromic acid or recovered manganese sludge (see p. 150), a condensation product is first formed which is then oxidized to the azine by the further action of the oxidizing agent :



Primary addition product.

o-*Phenylamino*-o-*tolyl-indamine.*

Safranine.

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[1] In the works, for practical reasons, enough aniline is taken to give equal molecules of aniline and *o*-toluidine.

In the early days of the manufacture of Safranine, an excellent oxidizing agent was made use of, namely, the recovered manganese dioxide obtained in the production of chlorine by Weldon's method. Later, as the Weldon manganese sludge disappeared from the market, use was made of chromic acid until the development of saccharine manufacture again placed large quantities of manganese sludge at the disposal of the dye manufacturers. It appears, however, that the Weldon mud cannot be altogether replaced by the manganese sludge from the manufacture of saccharine, so that at the present time the question is still unsettled as to the most advantageous method. As, however, the use of Safranine has also meanwhile diminished considerably, the question has now largely lost its importance (see also notes on Works Practice).

Mixture of Aminoazo-Toluene and Aniline.

54 gms. *o*-Toluidine.
24 gms. Aniline.
35 gms. 30 % HCl.
22 gms. 100 % $NaNO_2$.

54 Gms. *o*-toluidine ($\frac{1}{2}$ mol.) are mixed with 24 gms. aniline and then treated with 35 gms. of 30 % HCl. The mixture is cooled externally to 15° and diazotized at this temperature during 2 hours, with continuous stirring, by means of a concentrated solution of 22 gms. 100 % sodium nitrite, after which the mixture is warmed cautiously during 1 hour to 35°, and is then allowed to stand for at least 10 hours at 30°. 60 C.cs. water are then added, and the product run off from the salt solution, which still contains a little nitrite.

180 gms. H_2O.
180 gms. 30 % HCl.
About 100 gms. Fe.

The oily mixture of aniline and aminoazo-toluene is now treated with 180 gms. of 30 % hydrochloric acid and the same quantity of water, 100 gms. iron powder being then sifted in ; the temperature should remain below 25°.

The product is kept at this temperature until a test-portion, extracted with a little ether, no longer colours the latter solvent. If this is not the case after an hour a little extra iron is added. The fully reduced solution is now filtered and made up to 600 c.cs. This mixture, containing about one molecule each of aniline, *o*-toluidine, and *p*-diamine (mixture of phenylene- and toluylene-diamine) is treated with 110 gms. finely powdered chalk, and as soon as the evolution of carbon dioxide has ceased, the volume is made up with water and ice to 1 litre. The temperature must not exceed 0°. The mixture is now treated during 5 minutes with a solution of 100 gms. sodium bichromate in 400 c.cs. ice-water with stirring, which is continued for a further 12 hours. It is a good thing to leave the mixture over-night, after which it is boiled vigorously either by

110 gms. $CaCO_3$.

100 gms. $Na_2Cr_2O_7$.
400 c.cs Ice-water.

blowing in steam or by heating in a porcelain basin for half an hour. The product is then filtered through a large "nutsch" into a previously warmed jar, and the voluminous residue is washed out with half a litre of boiling water. The clear filtrate is precipitated by means of about 450 gms. salt, added a portion at a time, and the crude Safranine is filtered off after cooling. The colour is still rendered impure by the presence of various by-products, which must be removed. For this purpose the filter-cakes are dissolved in a litre of boiling water and a solution of 2 gms. sodium bichromate in 50 c.cs. of 50 % sulphuric acid is added cautiously until a filtered test-portion appears as pure as Safranine (blue shade). The whole liquid is then filtered, treated with about 15 gms. of dehydrated sodium carbonate (litmus should just be turned blue by the liquid after salting out), and the dye precipitated with 15 % of salt; it is then filtered off, pressed, and dried. *Yield of dry product about 40 gms.*

450 gms. NaCl.

About 1·3 gms. $Na_2Cr_2O_7$ in 40 c.cs. 50 % H_2SO_4.

About 15 gms. Na_2CO_3.

The product may be further purified by recrystallizing from water and alcohol. It is a good plan to stir up the moist press-cakes with their own weight of alcohol and then to dissolve up by boiling, a little water being added if necessary. *The yield of crystallized Safranine is about 25 gms.*

Notes on Works Technique and Practice.—The importance of Safranine has diminished considerably during recent years, and the price has fallen to such an extent that few factories concern themselves with its production. The reduction is also carried out by means of tin and hydrochloric acid, the tin being always recovered by means of zinc dust. With the old process, as already mentioned, the oxidation was effected with recovered manganese dioxide (in presence of oxalic acid). The purification of the dye was carried out by means of sodium sulphate.

The chromic oxide, which is mixed with considerable quantities of iron oxide, cannot be converted directly into chromic salts for tanning purposes, as is the case with that obtained from the manufacture of anthraquinone or of Acid Violet. It is therefore necessary to reconvert the dried residues from the filter-press into calcium-sodium bichromate by treatment with saltpetre and sodium carbonate. This process is carried out either in flat cast-iron roasting pans, or, better, in the well-known rotating oxidizing apparatus. (See, for example, *L. Wickop*, "Die Herstellung der Alkali Bichromate.")

The Safranines are still used to a fair extent for tannined cotton, and have also a certain importance for paper staining owing to their pure shade and their cheapness.

More yellowish marks are made from mixtures containing more or less aniline. If *p*-aminodimethylaniline (see Methylene Blue) be used in place of para-toluylene diamine, the bluish *Clematines* are produced which were formerly utilized in considerable quantities. As the Safranines possess at least one free amino group, they may be diazotized and coupled with various phenols and amines. In this way the important Indoines are formed which are strong basic colours and are used for cotton and wool under various designations (Indoine, Janus Black, etc.).

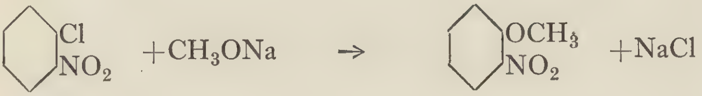
This will be a suitable point at which to make some further general remarks upon dyes, as in the case of the Safranines and related dyes especially, the conditions connected with their manufacture have altered very considerably in the course of time. It has already been mentioned that the choice of oxidizing agents for the production of Safranine has been dependent upon circumstances. The most suitable oxidizing agent for Safranine disappeared with the gradual diminution of Leblanc soda manufacture. Such more or less voluntary changes in the technology of the artificial organic colouring matters take place almost continuously before our eyes, and it is therefore very important for a colour factory always to possess some unfailing source of supply for any given product, and, on the other hand, to find sufficient outlet for all by-products.

I will give a few typical examples in order that the would-be colour-chemist may gain some idea of the importance of this aspect of the problem. In the short descriptions which have been given in this book we have become acquainted with various substances in the preparation of which always more than one main reaction product is formed. In this connection we are not concerning ourselves with inorganic by-products such as sulphurous acid, Glauber salt, or thiosulphate, but only with those organic compounds which it is customary to regard as the actual intermediates for the dye industry.

For example, in the manufacture of Cleve's acids and of the naphthylamine sulphonic acids 1:8 and 1:5 there is always a fairly constant ratio between the various isomers, which all have to be utilized. Only very occasionally is one forced to cast part of the reaction product aside until some satisfactory and profitable method of utilizing it is evolved. In the case of the acids mentioned above the position is very simple, as in the event of stocks of one of them accumulating, cheap azo dyes are produced with the aid of β-naphthol which may be either sold as such or in Black mixings.

The situation is not so simple in the case of *o*- and *p*-toluidine. When Safranine was utilized in very large quantities such accumulations of *p*-toluidine were obtained that the discovery of dehydrothio-*p*-toluidine came quite as a relief. Then, with the diminution in the demand for Safranine, such stocks of *o*-toluidine collected that cheap *p*-toluidine could only be obtained from the aniline-oil factories on condition that a certain quantity of *o*-toluidine was also taken, the price of which sometimes sank below 50 centimes. In a similar way the price of *m*-toluidine also fell below 1 franc per kilo., owing to the absence of demand. Then again, for a certain period, the toluidine question lost its importance as trinitrotoluene could be made from the *o*-nitrotoluene, which was used in large quantities as a shell-filling.

Another similar case is that of *o*- and *p*-nitrochlorbenzene ; for a long time the demand for *p*-nitrochlorbenzene was far in excess of that for the ortho compound. Then Sulphur Black T required such quantities of dinitrochlorbenzene that all the mononitro product was readily absorbed. The increasing competition in Sulphur Black T made the problem again acute, and large quantities of ortho-nitrochlorbenzene were amassed until the production of *o*-nitroanisole—

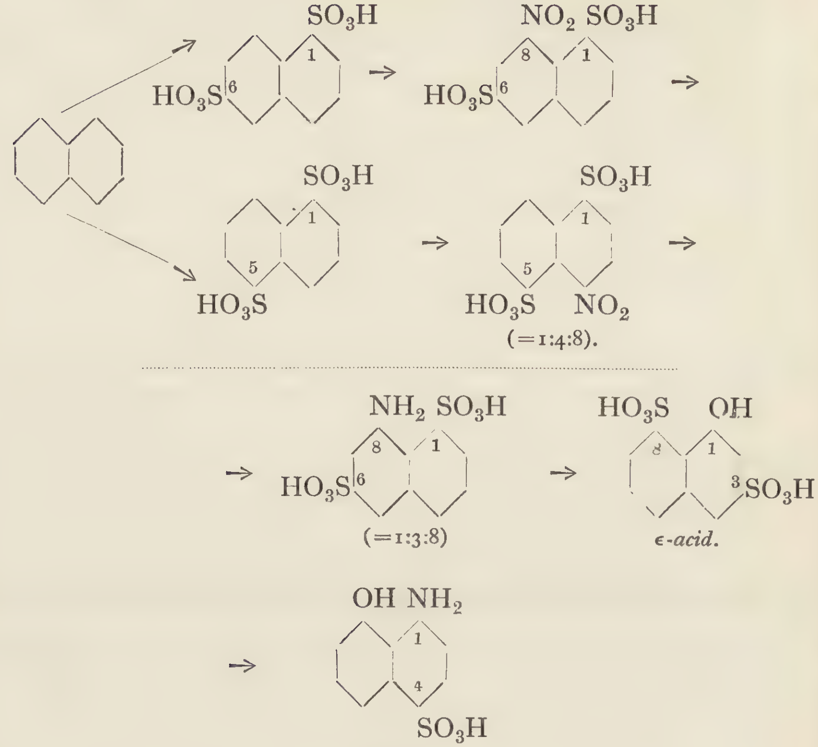


—for the preparation of *o*-dianisidine caused so great a demand for the ortho product that it became difficult to find sufficient use for the para product. Possibly the method for the preparation of *p*-nitraniline given on p. 72 may offer a way out of the dilemma.

Analogous cases are the simultaneous production of R-salt and G-salt, the formation of ortho- and *p*-nitrophenol, and so on. In many cases it is possible by suitable alterations in the method of manufacture to suppress one product (compare for example the two methods for the preparation of amido-G-salt given on pp. 35 and 36).

Again, aminonaphthol sulphonic acid 1:8:4, for instance, may be obtained *via* the naphthylamine sulphonic acid 1:8 (p. 30, III), or directly from naphthalene by disulphonation and nitration.

Reaction :



(=1:4:8).

(=1:3:8)

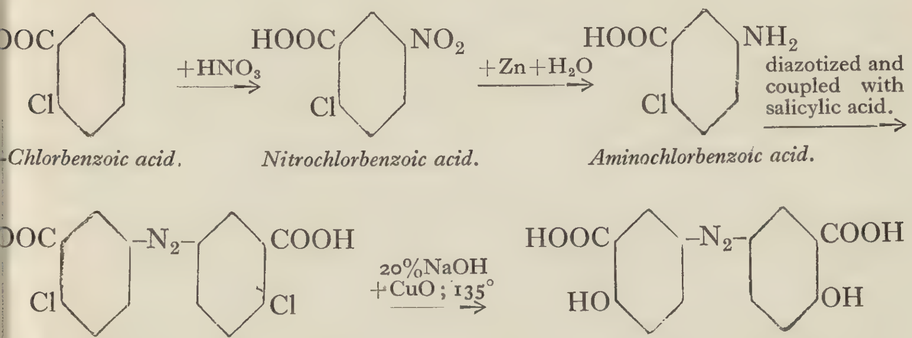
ε-acid.

S-acid.

A certain quantity of the β-nitro acid is formed at the same time which yields *naphthylamine disulphonic acid* 2:4:8 on reduction.

Other substances also may in time accumulate in such quantities that it becomes essential at last to make use of the ever-increasing waste-dumps, as only rarely is it decided to get rid of by-products simply by burning them. An interesting case of this is the neat method worked out by C. Mettler for utilizing the *o*-chlorbenzoic acid which is obtained in considerable quantities as a by-product in the manufacture of *o*-chlorbenzaldehyde. The resinous masses of crude *o*-chlorbenzoic acid finally attained the dimensions of a small hill, so that it was estimated that about 30,000 kilos. of pure *o*-chlorbenzoic acid remained unused for years. Attempts to convert the acid into anthranilic acid by treatment with ammonia and a little copper, or a cupric salt, by Ullmann's method, showed that the well-known B.A.S.F. method (from phthalic acid *via* phthalamide and oxidation with the exactly calculated quantity of sodium hypochlorite by A. W. Hoffmann's method) gave a much cheaper and purer anthranilic acid.

C. Mettler's device consisted in obtaining the hitherto unknown azo-salicylic acid by a roundabout way from *o*-chlorbenzoic acid, as it was certain from L. Oswald's experiments that this substance would possess remarkable dyeing properties. This interesting process is effected in the following way: nitrochlorbenzoic acid is obtained by the nitration of the *o*-chlorbenzoic acid; this is reduced with zinc dust in neutral solution to aminochlorbenzoic acid which is diazotized and coupled with salicylic acid and the chlorine of the valueless azo dye replaced by heating to 135° with caustic soda lye and a little copper oxide. In this manner azo-salicylic acid is obtained, the chrome lake of which is distinguished by its remarkable strength and great fastness towards light, milling and potting; it also levels admirably and has therefore become a very welcome addition to the pattern-card. The following formulæ will illustrate the reactions involved:



-Chlorbenzoic acid. *Nitrochlorbenzoic acid.* *Aminochlorbenzoic acid.*

Valueless azo dye. *Azo-salicylic acid = Erio Chrome Flavine A.*

It is not possible to obtain this compound by coupling aminosalicylic acid with salicylic acid, as this combination can only be effected directly to a very small extent (L. Oswald, *v.s.*).

These few, though characteristic examples, will suffice to show that with many dyes new problems will constantly occur according to the demand, which may in some cases take years to solve.

10. SUMMARY OF THE MOST IMPORTANT METHODS USED IN THE PREPARATION OF SYNTHETIC DYES

Sulphonations.

1. An aromatic substance is treated with concentrated sulphuric acid.
2. An aromatic substance is treated with sulphuric acid containing sulphur trioxide (Oleum).
3. By heating the acid sulphate of an amino compound to a moderately elevated temperature (Bake process).
4. Sulphonation with chlorsulphonic acid.
5. By converting a nitroso compound into the hydroxylamine sulphonic acid, and this in its turn into the amino-hydroxy sulphonic acid.
6. Replacing an easily removable chlorine atom in an aromatic substance by a sulphonic group, by heating with a sulphite.

Nitrations.

1. Direct nitration by means of concentrated nitric acid.
2. The substance to be nitrated is first sulphonated and the sulphonic group is then replaced by NO_2 by the vigorous action of nitric acid, frequently with the assistance of sulphuric acid.
3. By nitrosating an amine, oxidizing with dilute sulphuric acid, to the nitramine, which is then transformed to the nitro compound.
4. By heating a diazonium nitrate with dilute nitric acid.

Reductions.

1. Reduction with iron and water, in presence of much, little, or no acid, or in presence of caustic soda lye.
2. Reduction with hydrogen sulphide or with its neutral and acid salts.
3. Reduction by means of sulphurous acid.
4. Reduction by means of zinc, zinc dust, or tin.
5. Reduction by means of nascent electrolytic hydrogen.
6. Reduction with ferrous hydroxide (very occasionally).
7. Reduction by means of hydrosulphite (anthraquinone series).

Oxidations.

1. Oxidation with atmospheric oxygen.
2. Oxidation with chromic acid.
3. Oxidation with MnO_2 or manganese mud (Mn_3O_4).

4. Oxidation with sodium hypochlorite in alkaline solution.

5. Oxidation with nitric and nitrous acids.

6. Indirect oxidation, by chlorinating and subsequent treatment of the chloride with water.

7. Oxidation with lead peroxide (PbO_2).

8. Oxidation by means of nitrosyl sulphuric acid (Aurine, *Sandmeyer*).

9. Oxidation with ferric chloride (Helvetia Blue, formation of sulphones from sulphinic acids and *p*-diamines).

10. Oxidation with bichromate plus a ferrous salt (Safranine, Methylene Blue, etc.).

11. Oxidation in presence of an excess of one of the components used for a condensation (nitroso dimethylaniline in the preparation of Oxazines, for example).

Alkali Fusions.

1. Open melt with caustic soda, caustic potash, or mixture of the two.

2. Fusion with sodamide alone, or mixed with caustic soda and caustic potash (Indigo).

3. By heating with aqueous alkali under pressure.

4. Melting with alkali with the addition of an oxidizing agent (Alizarin, Indanthrene).

5. Fusion with lime (which in the anthraquinone series prevents the entrance of further hydroxyl groups).

Methods of Coupling.

1. Coupling is effected in the presence of sodium carbonate.

2. Coupling is effected in the presence of caustic soda.

3. Coupling is effected in the presence of sodium carbonate, caustic soda, or ammonia being added subsequently.

4. Coupling is effected in the presence of lime or magnesia, especially in the case of nitroamino compounds (*Sandmeyer*).

5. Coupling is effected in the presence of sodium acetate, to combine with the acid (the acetate may usually be replaced by the formate, but this requires subsequent neutralization).

6. Coupling is effected in the presence of mineral acid, either without neutralization, or the mineral acid is neutralized cautiously by means of sodium carbonate or acetate.

7. Very easily oxidizable substances may be coupled under a layer of petroleum (*e.g.* 1:5-dihydroxynaphthalene).

III. TECHNICAL DETAILS

11. VACUUM DISTILLATIONS IN THE LABORATORY AND IN THE WORKS

THE process of distilling under reduced pressure, commonly called Vacuum Distillation, is one of the most important operations in colour technology. Certain products are distilled under reduced pressure because they decompose at their boiling point under ordinary atmospheric pressure, and also because vacuum distillation offers certain other advantages. Owing to the lower boiling point, the radiation losses are smaller and, in addition, it is often possible to heat with steam instead of with fire, so that the apparatus may be placed wherever it is most convenient without any danger of fires. In addition, there is another very important circumstance which by itself often makes it desirable to distil various substances under reduced pressure, namely, the easier separation of mixtures composed of substances whose boiling points lie close together. Thus it is only possible to effect a satisfactory separation of the three isomeric nitro-toluenes by distillation in vacuo, and the alkyl-benzyl-anilines also can only be separated easily into their components in vacuo.

Whilst the fractionating columns used in the laboratory are for the most part of older and well-known forms, on the technical scale new and complicated pieces of apparatus have gradually been evolved. The older types of columns, in which the rising vapours had to pass through a downward stream of liquid by means of which they were washed or *dephlegmated*, are becoming obsolete, and are rapidly being replaced by more modern and efficient columns.

The principal of these new columns is as follows : The vapours must take as long a path as possible through the downward stream of liquid, but must meet with only slight resistance. Further, the stream of liquid must be finely divided, so as to offer as large a surface as possible for the interchange of the various high-boiling substances. At the present day there are two important types : First, the *Kubierschky* column, in which the gases have to take a zig-zag course,

PLATE XVI.

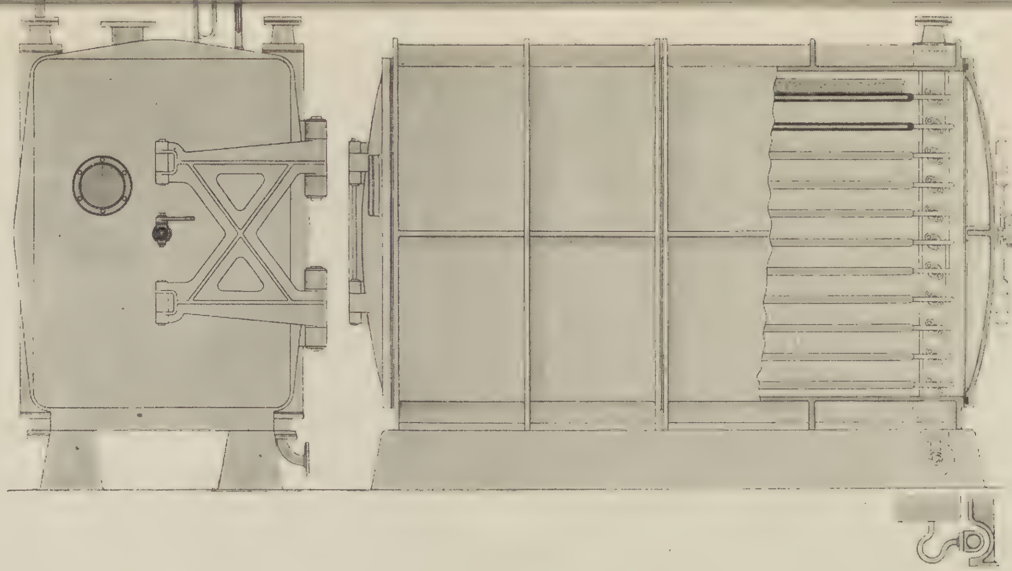


FIG. 40.—Vacuum drying chest for dyes (Passburg system) (scale 1 : 30).

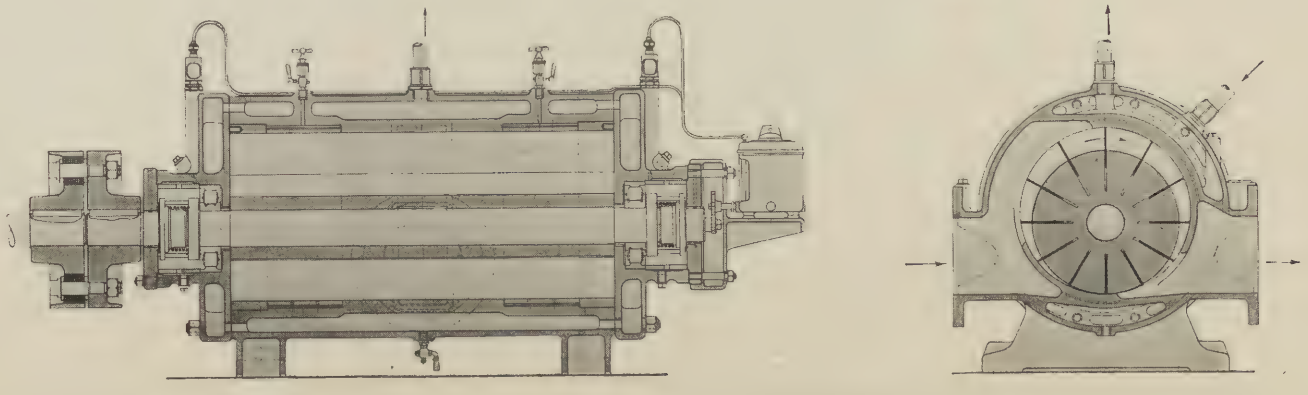


FIG. 41.—Rotary compressor and vacuum pump (made by the Swiss Locomotive and Machine Factory, Wintherthur) (scale 1 : 10).

during which they meet with a descending shower of liquid. Plate IX shows, in section, two forms of this extremely efficient apparatus. They are used not only for fractional distillation, but also for the removal of ammonia from gas-liquor, for obtaining bromine from Stassfurth mother-liquors, and for many other purposes. If it is used for distillation the upper opening is closed, the top portion of the column being cooled by spraying, whilst the remainder (9/10–19/20) is insulated.

The other form of construction, due to *F. Raschig*, consists in a tower filled with small cylinders, of equal height and diameter. On filling a tower with such cylinders they lie irregularly, as indicated in the drawing on Plate IX, so that the surface with which the gas and liquid come in contact is very considerable.

The vacuum is produced by means of a reciprocating pump, which brings down the pressure to about 50 mms. of mercury. Lower pressures down to about 8 mms. may be obtained by running two pumps in series. But here also there has been a change during the last few years; of late increasing use is being made of modern rotating pumps, such as the excellent pumps made by the Swiss Locomotive and Machine Factory in Winterthur, diagrams of whose compression and vacuum pumps (Witte's system) are shown on Plate XVI. The method of working is indicated by the diagrammatic sketch: the movable slides enclose a definite volume of air and drive it towards the exit-opening, by which means it is compressed. The machine is reversible, and may be used either as a compressor or as a vacuum pump, pressures being obtainable with it from about 4 atmos. down to about 12 mms. The machine must be cooled, as may be seen from the drawing. It is coupled up directly with an A.C. motor, giving 1500–2500 revolutions per minute, the loss of power on the transmission being almost negligible. As already mentioned, two rotating pumps are frequently coupled up together, one behind the other.

Where it is desired to subject liquids to a vacuum distillation, an ordinary boiler is made use of, which is frequently of very large capacity. For instance, as much as 20,000 kilos. of aniline may be vacuum distilled in a boiler which is heated by means of several steam coils. The case, however, is different when dealing with β-naphthol or a similar product, and such large quantities cannot be distilled at once. Quantities of 2000 kilos. and over can indeed be dealt with, but a different type of apparatus is required. The high boiling point of β-naphthol prevents steam being used for heating, although here also very promising experiments have been made with the

Frederking apparatus. Normally the heating must be done by direct firing, and for this purpose gas heating is the most satisfactory, owing to the ease with which it can be regulated. Very often the use of an oil-bath is omitted, but in this case there is the risk of the residual pitch becoming charred, so that it is difficult to remove it from the still, and it ceases to be of commercial value.[1] On the large scale it is unnecessary to introduce air during a vacuum distillation, as " bumping " does not occur. It is, however, necessary for the whole apparatus to be well insulated, and also that all tubes in which stoppages might occur shall be easily accessible and capable of being heated ; the receiver must be provided with a jacket both for heating and cooling. After the distillation is finished the residual liquid is blown out of the still through a tube into closed-in moulds to avoid the inconvenience of any escaping vapours. A large empty boiler is placed between the pump and the receiver, in order to catch the water and any sublimate which may be formed. Particularly in the case of β-naphthol, large quantities of the product are carried over as a fine snow which would stop up the pump.

With such large apparatus several thermometers are required ; one goes to the bottom of the still, thus permitting the temperature of the crude mixture to be ascertained, so that it is possible to recognize when the distillation is just beginning and when it is coming to an end. When the difference in temperature between the vapours which are distilling over and the residue in the still exceeds 50°, the process should be stopped, or else the pitch will be charred.

The illustration on Plate X shows an installation for the distillation of β-naphthol ; it is heated by means of three gas-rings, and is calculated for a charge of 1000 kilos. ; such a distillation should occupy about 4 hours. The pitch constitutes about 5 % of the crude naphthol. The naphthol is allowed to solidify in moulds like sugar-loaves, and after disintegration it is " whizzed."

For liquids, worm-condensers may be used, or straight tubular condensers containing from 20–30 tubes. Condensers of this type may also be heated in order that diphenylamine or other easily fusible substances may be used with them if it is preferred not to distil them with steam (see p. 99).

Frequently also an observation window is placed in the vertical portion of the condenser, through which the stream of liquid may be accurately observed.

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[1] Naphthol pitch is an important commercial product. It is a black, brittle mass with a vitreous lustre, which is used as an insulating material for covering the joints of electric cables.

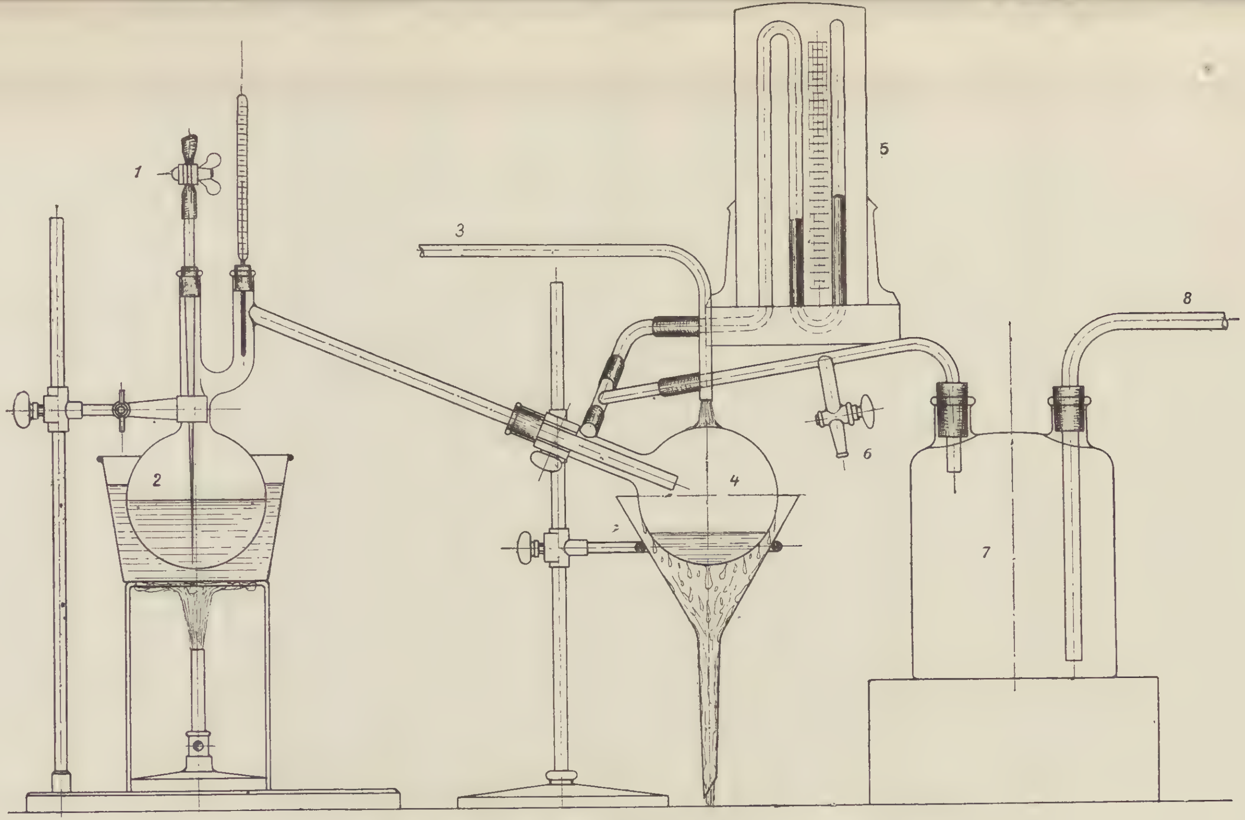

FIG. 27.—Diagrammatic arrangement for a laboratory vacuum distillation.

1. Screw clamp for capillary. 2. Capillary tube and Anschütz flask. 3. Cooling water. 4. Receiver. 5. Manometer. 6. Safety tap. 7. Safety bottle. 8. To vacuum pump.

For laboratory use the arrangement shown in Fig. 27 works very well. The distilling flask possesses a double neck, one for the fine capillary and one for the thermometer, and at the same time this arrangement prevents the contents from spurting over. Heating should never be done directly, but always by means of an oil-bath, the temperature of which is 30–40° higher than the distilling temperature. The capillary is drawn out from an ordinary thin glass tube, and should be soft and flexible like a silk thread ; it should just touch the bottom of the flask, and the upper part should be closed with a piece of pressure tubing and a screw pinch-cock. Just enough air should be allowed into the flask during the distillation to keep it going quietly.

An ordinary distilling flask with a long neck is used as a receiver, and not any complex piece of apparatus. If several different fractions are to be obtained, the distillation is stopped for a moment and the receiver changed, which occupies only a few seconds. The method of cooling may be seen from the sketch. The manometer is not placed in the pump circuit, but is attached to a separate tube in order to prevent any liquid from getting into it. The safety tap shown is of some importance, as it permits the introduction of a little air if the liquid in the distilling flask begins to show signs of frothing over ; by this means any distillation may be carried out in a short time. The pump should be separated from the distilling apparatus by means of a large safety bottle. It is advisable that the water-pump be connected to the main supply pipe, in order to be independent of variations in pressure.

Method of carrying out the distillation.—The oil-bath is heated up to the correct temperature and the pump started. Usually a little water or solvent comes over first, so that the vacuum must be reduced by means of a safety tap. After a time the product becomes quietly fluid, and the capillary is regulated so as to allow a vigorous stream of very small air-bubbles to pass through. After a time the distillation begins, which offers no difficulties in the case of liquids, but the side tube tends to become stopped up in the case of solid products, such as β-naphthol, naphthylamine, etc. For this reason the neck of the flask is heated up before the beginning of the distillation, so that the first drops may be superheated. Sometimes it may even be necessary to heat up the portions where the corks are by means of a Bunsen flame, in order to force the distillate to pass over. With good quality resistance glass there is no danger of cracking, but at the same time it is always advisable to wear a pair of safety goggles. The distillation should always be carried out quickly ; for example, 200 gms. β-naphthol can be distilled in 15–20 minutes, the receiver being kept moderately cool. The manometer is isolated from the rest of the apparatus, and is only connected up from time to time to test the vacuum. Beginners often daub their apparatus with paraffin, collodion, and other substances, in order to make them airtight, but this is quite unnecessary. The simplest method is to take good quality corks and to soak them well in hot, hard paraffin-wax beforehand, which renders any further treatment unnecessary. It is only necessary to use rubber stoppers when working with a very high vacuum, though for this purpose an apparatus that has been blown together is still better.

The distilled substance is melted by heating over a bare flame, and the liquid is poured into a small porcelain dish. The solidified product is pure and should not be further recrystallized.

12. NOTES UPON THE CONSTRUCTION AND USE OF AUTOCLAVES.

Autoclaves or pressure vessels are always used in cases where it is necessary to raise the temperature of a substance above its boiling point, or where gases are evolved on heating, which are necessary for the reaction. In this connection the most important substances dealt with in colour technology are aqueous solutions and mixtures, and after that alcohol and alkyl chlorides. The limits of pressure and temperature are about 60 atmos. and 300° C. Generally speaking the ordinary type of apparatus is not calculated to withstand greater stresses than those indicated.

Both vertical and horizontal autoclaves are made use of, either with or without stirring-gear. If the mixture is homogeneous, stirring is unnecessary; but if several layers are formed, or it is necessary to bring together solid and liquid substances, then continuous stirring is essential. As an example of a reaction carried out under pressure in which stirring is unnecessary, the ordinary preparation of dimethylaniline may be given; whilst all alkali-fusions afford examples where continuous stirring is requisite.

The autoclaves used are hollow, cylindrical vessels of 100–10,000 litres capacity, provided with a flange to which the cover is affixed by means of nuts and bolts; for the sake of greater strength, the bottom is usually made hemispherical. They are almost invariably made of iron, either cast iron or cast steel being used, the latter offering the greater measure of safety for working at high pressures (see also steel and iron as structural materials). Besides cast iron and steel, tin is also used ; autoclaves made of tin are manufactured, having walls up to 40 mms. thick ; they are either riveted or autogenously welded. The objection taken to welded autoclaves by many colour factories is quite unjustified, and is explained simply by the fact that at first the welding process had not been fully perfected.

The screw-bolts form the weak point in every autoclave, and they must therefore be made from the best hand-forged wrought iron. The cover has flange-pieces cast on, as indicated in Fig. 32. These serve for affixing the armatures and the stuffing-box of the agitator. The bracket which bears the agitator should be high enough to make it easy for the packing of the stuffing-box to be looked after and renewed. The stuffing-box itself, through which the axle of the stirrer goes, should be as simple as possible, and cooled with water. Hollow stuffing-boxes are also cast, through which water may be circulated. Cooling by means of circulating oil, such as is done with success in the case of steam turbines is here unnecessary, as the conditions are quite different. The cover is provided with two manometers and two thermometers, together with two safety valves. Of recent years it has become the custom in certain cases, with the approval of experts, to do away with the safety valves, as these never work properly and are a constant source of annoyance. By using two thermometers and manometers it is easily possible to follow the course of a reaction exactly. With large autoclaves the cover is provided with a special opening or man-hole, this alone being opened from time to time as occasion requires. The joint between the cover and the body of the vessel is made tight by means of a special packing ring let into the flange of the autoclave itself, suitable materials for the ring being copper, lead, lead-covered iron, or asbestos board. The rings must be accurately turned, and must have a width of 20–50 mms. and a thickness of 1–6 mms. Lead is somewhat easily squeezed out by the pressure of the screws, but withstands ammonia very well ; copper is the ideal packing, but is attacked by ammonia. Asbestos can be used for low pressures, but has the disadvantage that it nearly always tears when the autoclave is opened. The cover is screwed on by first tightening lightly diametrically opposite bolts, and then working round in a circle, always screwing up tighter and tighter, the final tightening being effected by hammering the long wrenches employed for the purpose ; there is no danger of the bolts being broken off in the process.

The walls of an autoclave should never be brought into contact directly with the substances under reaction, as every melt attacks the walls, so that after a time the apparatus becomes too weak and must be taken down. For this reason a lining is nearly always inserted in the actual pressure-vessel, and is kept in position by pouring in solder. It is not permissible simply to place the liner in the autoclave as the heat transmission is inadequate and the walls of the autoclave may become red-hot. When placing the liner in position the latter is fixed immovably in the autoclave by means of a strong girder, and then the solder is poured in through a sheet-iron funnel. Enamel and lead may be protected by covering the inside of the liner with wet cloths, or it may be filled with water which must, however, be heated up and afterwards cooled by means of a worm. If the heating be omitted it is quite possible for the solder never to reach the bottom, but to solidify half-way down ; if, on the other hand, the inner vessel be cooled by water without using a coil, then the water will boil away altogether. An inadequate heat transmission may be caused, however, not only by the presence of air in the intervening space, but still more by the formation of crusts of salts on the inside of the vessel. In cases where salt separates out, stirring must be effected continuously, and the stirrer must approach the walls as closely as possible, in order to keep these scraped clean. If, however, large quantities of salt have separated out no amount of stirring will be of any use. A case is known to the writer where, owing to the formation of a crust of salt only 4 cms. thick, an autoclave became heated up to redness, and with an internal temperature of 240° and a pressure of 48 atmos., blew out like a balloon, after which the bottom split open. The issuing stream of vapours cooled the steel sufficiently to prevent any further danger. It is quite certain that if cast iron had been used it would have exploded.[1]

For the reasons just given, it is always desirable to heat the autoclave, whenever possible, in a suitable bath. Such a bath may contain either oil or solder. Even when no crusts are formed, which would interfere with the heat transference, phenomena occur at higher temperatures, which render the use of a solder-bath very desirable. The solder which is poured in to fix the liner in position always liquefies if the autoclave is heated directly, and the liner rises up until finally it touches the cover, and so, after cooling, renders it difficult to screw the cover down tightly again when closing the vessel. In this way strains are developed in course of time which make the autoclave leaky, and, in addition, the strain on the bolts is a serious source of danger. With incorrect heating not only does the autoclave itself suffer, but also the substances which are being heated ; such cases have been discussed in detail in connection with α-naphthol and β-naphthylamine.

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[1] The β-naphthol melt is an example of this type, and any attempt to carry out this melt without the use of a metal bath will with certainty ruin any autoclave.

The autoclave is charged either through the man-hole, this being then carefully closed, or, if possible, the substance is sucked in by evacuating the vessel so that as little opportunity as possible may be given for the development of leaks. Water expands very considerably upon heating (according to Mendeleef by 20 % of its volume on heating from 0–250°), for which reason no autoclave should be filled up to more than 80 % of its total volume. If the vessel is completely filled such an enormous pressure will be developed that it will be burst open. It is therefore necessary to have a notice above every autoclave, showing clearly the total volume, the maximum pressure, the maximum filling, and the method of charging.

The calculations for an autoclave are matters for engineers who have official standards upon which to base their estimates. It is, however, also advisable to have every apparatus recalculated in a first-class engineering works, after which the official sanction for the scheme may be applied for.

By means of a travelling crane the autoclave is placed in its masonry setting, which has already been erected, and which should be held down by means of iron rods placed about 30 cms. apart, the projecting ends being screwed down to the brickwork by means of iron plates 25 by 25 cms. square. The autoclave or its bath is placed in a counter-sunk ring, as shown at the bottom of Fig. 32, and the apparatus, after being charged, is heated up by means of good coal. If the setting has been correctly done, it is unnecessary to carry out the first heating with excessive caution, although it is always advisable to start with a small flame. The fire-bars must be kept clear, and, if necessary, one or more should be removed if the draught is insufficient. It is also advisable to have a separate chimney for each pair of large autoclaves, so as to be independent of neighbouring plant. When working on the large scale the heating-up always occupies several hours, but once the brickwork is hot a very little wood or coal will suffice to keep the temperature up. For temperatures above 200° the heat losses by radiation are so considerable that the portion of the apparatus projecting from above must be insulated by means of a tin cover lined with asbestos. To cool, the cover, which is made in several pieces, is removed, and at the same time the furnace door and the dampers are opened. By blowing off a portion of the contents into the air, or in the cases of alcohol and ammonia, into the condenser, the cooling of the autoclave may be greatly accelerated without the brickwork losing too much heat, which is of importance for the next operation. Whilst a melt is being carried out the autoclave must be carefully watched. The temperature of the oil-bath should be about 30° higher than the internal temperature, and the two thermometers and manometers should agree within a couple of points. If greater deviations are shown, the thermometers must be checked, and in some cases the process must be interrupted.

By the use of pyrometers it is possible to superintend the running of a process from the laboratory, and self-registering manometers are coming into use which permit of the subsequent examination of the pressures for purposes of control. A book should be kept in which all happenings are entered, so that documentary proof is always available in case of a break-down or an accident. If, in spite of all precautions, any serious mishap should occur, such as an unexpected rise of the temperature or pressure, the fire must be raked out at once, all the dampers and flues should be opened, and all the *personnel* should be evacuated from the shed in which the autoclave is situated and from the surrounding buildings. The explosion of an autoclave, like one of those shown in Figs. 31 and 32, may lay an entire factory in ruins. Since, however, all autoclaves are made with an eight-fold factor of safety, there is really no danger with proper attention. Every year each autoclave is examined by a boiler inspector, being cleaned out and well cooled for the purpose. The inside of such a vessel must not be entered until it has been shown that a candle can burn quietly therein. Usually only the man-hole is open, and compressed air is blown in. Never less than two workmen should be engaged upon the job. The result of the examination should be made the subject of an official report. Frequently the lining is removed in order that any alterations in the wall may be accurately measured; the liner is removed for the purposes of the examination by lighting a fire inside, which is kept going by means of compressed air. As soon as the lead is molten the liner rises up somewhat and is then removed by means of the crane. The lead is removed by means of iron ladles and is cast into bars.

Autoclaves are generally erected in tall, well-lighted sheds provided with a travelling crane. Plate VII shows in section the interior of a colour shed with the adjoining autoclave shed. It may be seen from this how the materials are brought to the vessel, and how the finished product is blown over directly into the intermediate shed.

Laboratory Autoclaves are constructed on precisely similar lines to those used in the works. The diagrams on Plates I and X show two vessels made from cast steel with and without stirring gear. Plate XIII also shows all the details of a properly constructed stirring-autoclave. As already mentioned, the liner must be very carefully fixed in by means of solder. If a solder-bath be used instead of oil, an iron bath must be provided, as copper is attacked by the lead. In the laboratory the stuffing-box is not usually cooled, as the loss by possible blowing off is very slight ; it is only advisable to cool where high pressures and temperatures are encountered, but for such cases it is preferable to use the rotating autoclave already described. Attention may be called to the fact that the stirrer should always work clockwise, to avoid unscrewing the nut of the stuffing-box. The nuts which close the autoclave are tightened carefully and regularly in the laboratory, just as is done on the large plant, with the difference, however, that it is inadvisable to tighten up the nuts with a hammer, as they may be broken off. It suffices to tighten up by means of a long spanner, the autoclave being placed in a stand which will prevent it rotating.

The cover may be either dome-shaped or flat, as may be seen from the sectional diagram of Fig. 34 and from Plates I, XIII, and XIV, Fig. 35. The flat top is to be preferred as it is easier to screw the agitator bracket down to it firmly, and the flange-pipes can more easily be rendered air-tight. The vertical autoclave shown on Plate XIV, Fig. 35, has a domed cover with flange-pieces for affixing the various fittings.

The heating is done by means of a Fletcher burner, and, later, it may be done with a good Bunsen burner directly under the middle, but not by several burners on different sides. The autoclave must be protected from draughts and be insulated by a tin cover, about 70 % of gas being saved in this way. In order to cool, the whole apparatus is removed from the bath and is stood on an iron triangle, so that the oil may run back into the bath. Heating and cooling will occupy only about an hour. In the event of anything unforeseen occurring the same rules apply as on the large scale, making due allowances for the different circumstances. The screws must not be loosened so long as there is any pressure, but that on the stuffing-box may be moved without danger. For the rest, attention is called to the general rules given below.

Instead of using an enamelled liner, it is also possible to have the cover and the inside of a laboratory autoclave enamelled directly, but there are few factories which do this satisfactorily. The cost

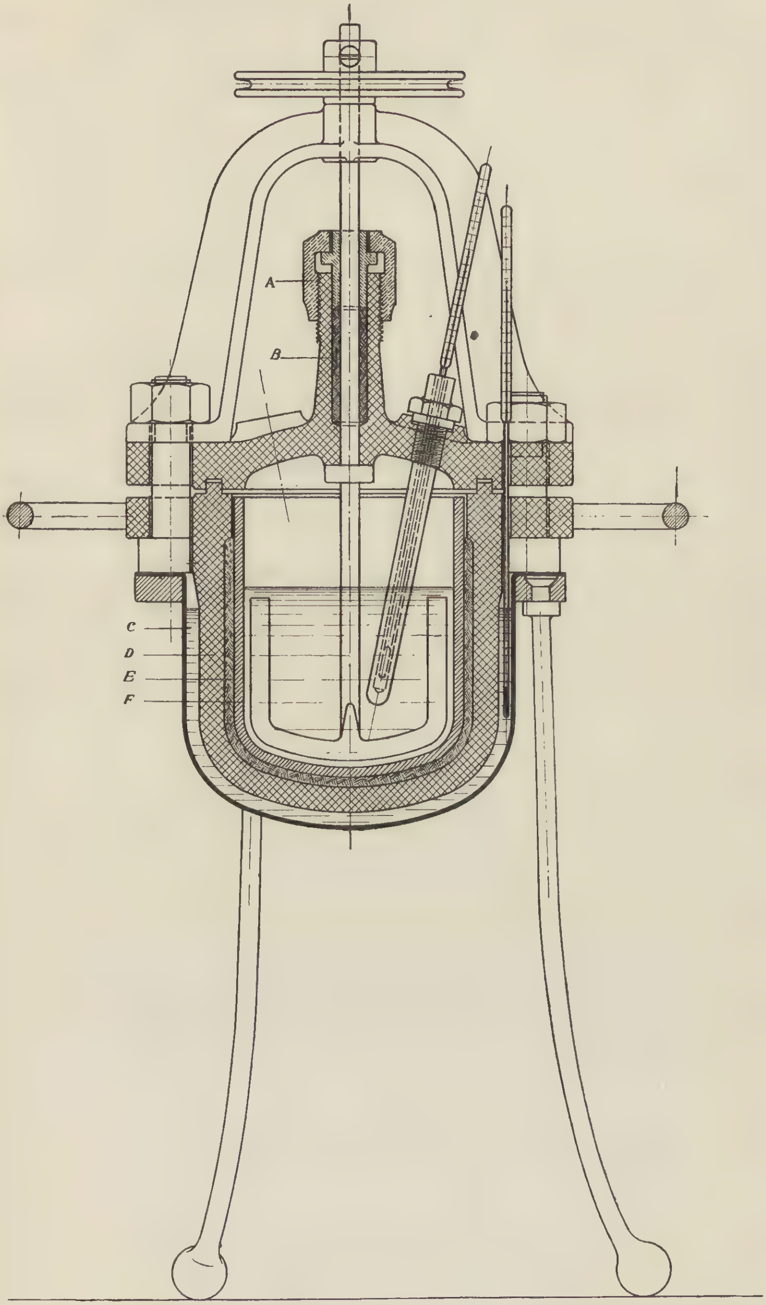


FIG. 34.—Section through a laboratory autoclave.
A. Stuffing-box. *B*. Packing. *C*. Oil-bath. *D*. Cast-steel vessel. *E*. Lead. *F*. Liner.

of the enamelling is calculated according to the weight of the apparatus.

In those cases where it is necessary to carry out an operation under pressure in the laboratory with stirring, considerable difficulties are found when pressures of about 20 atmos. are reached, as it is necessary to tighten up the stuffing-box and also to cool it. For this reason I have made use for many years of a piece of apparatus which is similar in construction to the known form, but has also certain novel features. Plate XV, Fig. 37, shows such a rotating autoclave in use, and Fig. 38 shows it in section.

The opening is contracted so that as few bolts as possible may be required, the whole vessel being turned in one piece from an old wrought-iron printing roller. In order that the pressure and the temperature may be measured, the apparatus is arranged diagonally, and the angle of inclination may be altered as desired. The top opening is utilized for the manometer, and the bottom for the thermometer, which is fixed in by means of asbestos paper. The weight of the autoclave does not rest upon the axle of the worm-drive, but is taken up by a bronze stuffing-box which is attached to the supporting columns. For this reason surprisingly little power is required to drive it. For a content of 400 c.cs. the apparatus weighs 11 kilos., and is constructed to stand 100 atmos. pressure; the stand weighs as much again. Whilst it is being heated, the cylinder is covered with a tin cover, so that less than 20 % of the gas is needed which would be required by any other form of autoclave. Experiments made with a view to replacing the expensive bolts and nuts by a simple screw fastening have met with no success, as at about 180° the screw packing always blows out. The packing simply sticks to the cover on screwing up, and it is impossible to make the apparatus tight.

General Rules for the Use of Autoclaves.

1. The packing ring must always be clean.

2. Tightening up must always be done at diametrically opposite points by first screwing up the bolts gently, and then tightening up by working round in a circle.

3. If neutral or similar liquids are heated, which evolve no ammonia, manometers fitted with bronze tubes may be used. If, however, vapours are given off which attack copper or bronze, a steel tube manometer must be used, as copper and bronze are soon destroyed.

4. A liner fixed in position by means of solder must always be

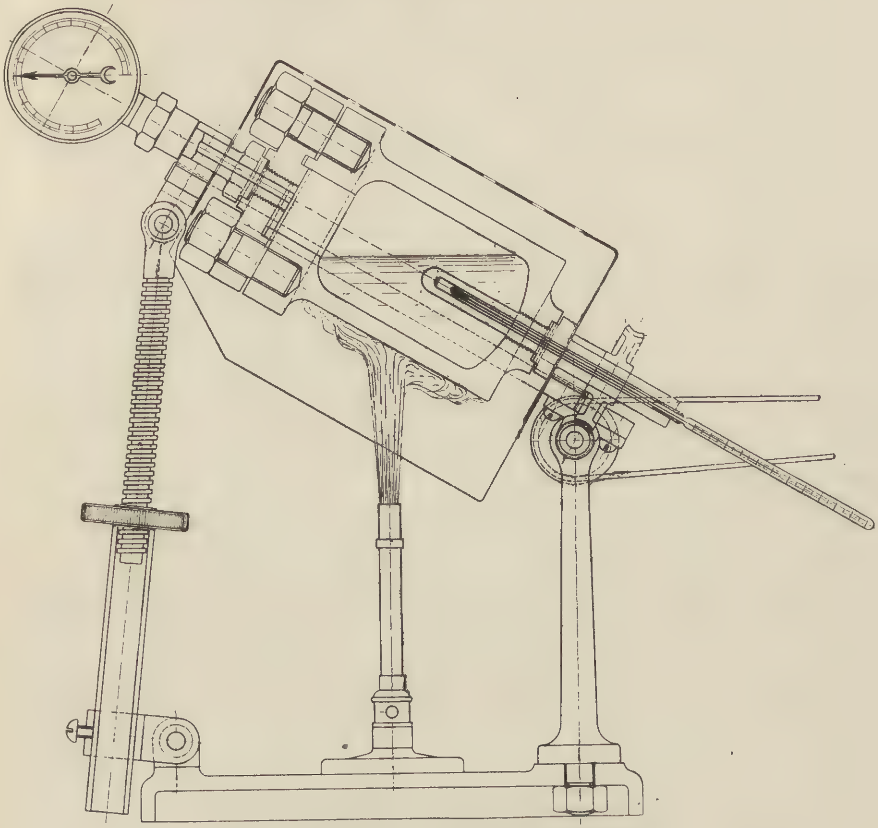


FIG. 38.—Section through rotating autoclave.

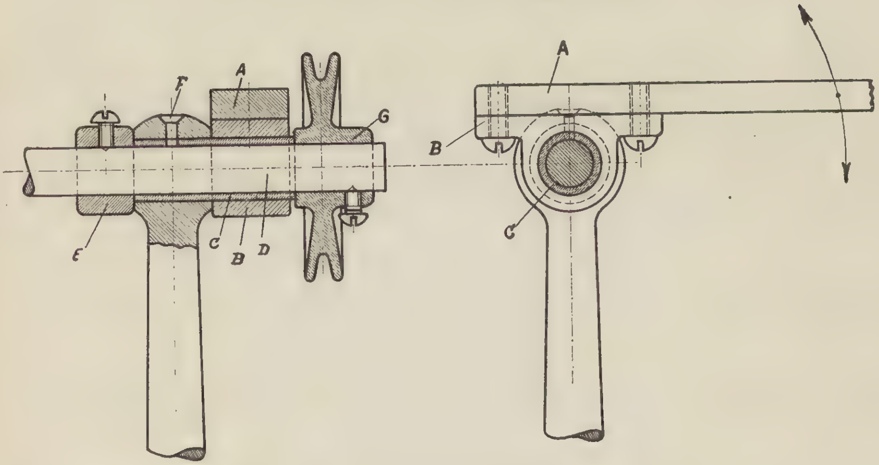
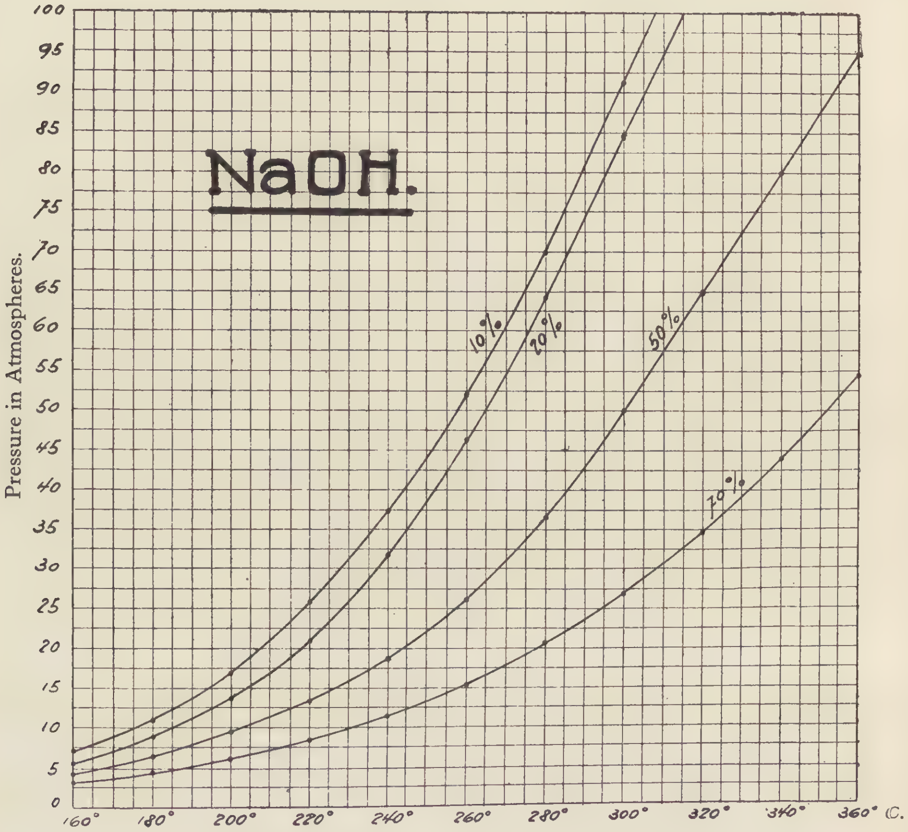


FIG. 38A.—Details of rotating autoclave.
A. Frame supporting autoclave. *B*. Hinge. *C*. Bronze bushing for axle. *D*. Worm shaft. *E*. Collar. *F*. Oil-hole. *G*. Bronze pulley-wheel.

used; any solder which is squeezed out being replaced. Only under quite special conditions can the use of a liner be dispensed with.

5. The temperature must be measured both inside and in the oil- or metal-bath, the latter temperature being about 25° higher than the former.



Temperature-pressure curve for aqueous caustic soda.

6. The autoclave must be protected from draughts, for which purpose it should be insulated and, on the large scale, provided with a cover.

7. If the vessel is found to leak, the experiments must be stopped. The screws must not be tightened so long as there is any pressure; the stuffing-box, however, may safely be tightened up during the course of the process.

8. An autoclave may only be opened after the pressure has been

blown off, as the manometer often fails to indicate a pressure, although it may be present.

9. Neither the vessel nor the oil-bath may ever be completely filled, as both water and oil expand very considerably on heating. If the vessel is completely full it is certain to burst.

10. Every autoclave should be officially examined annually, tested, and a report made on its condition. The date of examination should be stamped on the vessel. Both the capacity and the maximum pressure allowable should also be marked.

11. Works autoclaves should be thoroughly cleaned out, cooled, and provided with a ventilating tube before the examination.

12. The stonework for a works autoclave should first be erected on firm foundations, and then the complete autoclave should be lowered into it. After it has been mounted the apparatus should at once be ready for use.

13. STRUCTURAL MATERIALS USED IN DYE CHEMISTRY.

The destructive action of chemicals makes the nature of the structural material used in the dye industry a matter of prime importance. From time to time it becomes necessary to decide what material is to be used, and experience, or, if one may say so, chemical instinct, must be called upon for guidance.

The materials used in colour technology may be divided into Inorganic and Organic. The Inorganic may be subdivided into Metals and Non-metals, and the Organic into Natural and Artificial.

1. *Metals.*

Iron is the most important structural material used in dye chemistry, and is utilized in every variety and form.

In the form of *cast iron* it is used for sulphonating- and nitrating-pots, for evaporating plant, cocks, stirring-gear, autoclaves, and, in short, wherever the liquids dealt with are neutral or alkaline. The insufficient tensile strength of this excellent and easily cast metal alone prevents its still wider use.

As is well known, the properties of cast iron vary considerably according to its chemical composition. For *acid-resistant cast iron*, that is to say, such as is little attacked by concentrated acids, ordinary grey cast iron is made use of, its resistance being improved by certain additions which are kept a secret by the various foundries.

Ordinary grey cast iron answers all requirements when dealing with sulphuric acid of at least 75 % strength, nitric acid, or mixtures of the two. It becomes passive, and so acquires quite a fair resistance even to moderately dilute acids. It never does, however, to trust to luck in these cases, and experiment alone can decide whether grey cast iron will do in a given case. Further, the vessel must be carefully cleaned out after every stoppage. Grey cast iron vessels must be washed out when a manufacture is stopped, traces of acid removed with boiling soda solution, the washing water blown out at the boiling-point, and the small remainder swabbed out so that the vessel is completely dry. If the pot stands in a wooden water-bath, then the latter must be kept filled to prevent shrinkage, and the water should be made strongly alkaline by means of soda to prevent it becoming foul.

Further, the agitator brackets of vats, autoclaves, and other vessels are constructed from grey cast iron. To ensure easy running the toothed wheels should be well oiled, and it is also very advisable for all larger pieces of apparatus to be mounted on ball-bearings whenever possible, as by this means a considerable saving of power and lubricant is effected. The stands and end-pieces of filter-presses are made of cast iron, but not the tie-rods, as cast iron has not sufficient tensile strength for this purpose. Autoclaves may be made from cast iron for working up to 40 atmos., but for higher pressures cast steel must be used, as cast iron is liable to contain blow-holes when used on too large a scale and, further, the walls required would be far too thick. The autoclave shown on Plate XII (Fig. 32), constructed of cast steel, has walls 80 mms. thick, and weighs 10 tons; to construct a vessel of similar capacity with a diameter 1·2 metres of cast iron, and capable of withstanding a working pressure of 40 atmos., it would be necessary to make the walls 400 mms. thick, and its weight would be over 60 tons. Such a freak apparatus could not in any case be used technically, owing to the enormous tension which would be produced on heating. The fusion-pots for the manufacture of naphthol are also made of grey cast iron, and it has been found that the addition of 1–3 % *nickel* increases the resistance to alkali to a remarkable extent; fused alkali, especially caustic potash, attacks iron very strongly.

A type of cast iron which is completely, or almost completely, unattacked by acids has been on the market fairly recently in the form of alloys containing about 12 % *of silicon* and 4–6 % *aluminium.* This ferro-aluminium silicon alloy is, however, somewhat strongly attacked by hydrochloric acid; it was first made use of in England under the names of *Ironac* and *Tantiron;* there are also certain imitations known as Kieselguss, Azidur, and Clusiron, which can all be cast very easily but are unfortunately glass-hard and brittle, so that they have to be worked with an emery wheel. For nitric acid distilling plants these alloys serve excellently, and they also form a welcome addition to the list of materials available for various other special purposes, but they cannot be used for the linings for autoclaves owing to their brittleness.

Where great strength is necessary, wrought iron, ingot iron, and steel must be used. These forms of iron are used for the tie-rods of filter- and hydraulic-presses. The head-pieces of the latter must be made of cast steel, as cast iron has not sufficient strength. In recent years also Swiss electric steel has been used. Steel is also used for the spiral tubes of spring manometers where ammonia is dealt with. Ingot iron is employed for the hoops of vats.

Formerly, rather more use was made of *copper* than at present, but even to-day it is quite indispensable. It is used for scoops (but not for ordinary diazotizations), for the baskets of centrifuges, for piping, and, in particular, for drying trays, where it is used almost exclusively. It is not resistant towards ammonia admixed with air, and is often tinned in order to protect it. Alcohol stills are usually made of copper.

Tin is hardly used at all as such, but only in the form of alloys, such as bronze, lead-tin alloy for filling baths,[1] and, especially, for tinning iron and copper vessels [2] (see homogeneous lead coverings).

Zinc, also, is rarely used as such, but chiefly in the form of brass and bearing-metal alloys, and also as the coating of the so-called "galvanized iron."

Aluminium, on the contrary, owing to its great resistance towards dilute and concentrated nitric acid, is coming more and more into use. It is frequently met with in the form of piping for nitric acid and for nitrating pots, but it has the disadvantage of offering only a poor resistance to factory air.

Nickel is hardly ever used except in special alloys.

Of other metals than iron, *lead* is by far the most important, and is quite indispensable. It is found in nearly all filter-presses in the form of lead tubes, and also for other piping which has to deal with acid and alkaline liquids. The head-pieces of the filter-presses are covered with sheet-lead, as also are the inlet tubes. It is often found on heating metal which has been covered with lead that the latter becomes loose, develops large blisters, and finally breaks away. This disadvantage is overcome by fusing or alloying the lead covering to the metal beneath, instead of merely laying it on. Apparatus which has been covered with an intimate coating of lead in this way is said to be *homogeneously lead-lined;* this homogeneous lead covering is playing an increasingly important part in colour technology. Circular apparatus such as the lining for autoclaves, and so on, is lead-lined according to the method of Kühnle Kopp and Kausch by rotating the vessel rapidly and then pouring in lead. In this way all the pores of the metal are completely closed, and it is possible to deal with plant up to 6000 litres and weighing up to 10 tons. Iron and copper, before being treated in this manner, must first be tinned, otherwise the coating does not adhere well. This layer is often quite thick, 2 mms. and more, so that several thousand kilograms may be required for a large piece of apparatus.

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[1] An alloy made with equal parts of lead and tin does not expand at all, practically speaking, on heating.

[2] The inlet-pipes of filter-presses, and also the cocks of colour vats, are practically always made from the best quality bronze.

These short notes do not, of course, in any way exhaust the uses of metals in the dye industry, but they suffice to show what a large part is played by these structural materials in the industry.

2. *Non-Metals.*

The most important of the inorganic materials are cement and stoneware.

Where complete resistance to acid is required, *stoneware* is the only material which can be used. Occasionally, indeed, its place may be taken by lead, but, as every works chemist finds out in course of time, even with the most careful lead-lining, expensive repairs become necessary sooner or later. If a plant has to be used for an indefinite length of time without interruption, stoneware must be used or, very occasionally, acid-resistant stone, such as volvic lava, granacite, or Binger sandstone.

For smaller-sized plant, taps made of stoneware are much used, and with careful treatment they will last indefinitely. They are liable, however, to be damaged by hot liquids owing to cracking; they must also be carefully lubricated to avoid sticking. The so-called armoured stoneware cocks are more resistant to shock and heat; the outside consists of lead-lined tin-plate which is usually tightened up by means of a screw, so that by loosening the latter slightly the tap is readily removed. These armoured taps have quite replaced the older type made of hard lead (lead-antimony). Stoneware is also used for piping, centrifuges and valves. The baskets of stoneware centrifuges are placed inside a steel basket to prevent them flying to pieces owing to the centrifugal force. Some of the pieces of apparatus made are very complex, but we cannot go further into this question here; details will be found in the catalogues issued by the stoneware manufacturers.

Stoneware reservoirs are much used which are either made in one piece or built up from separate pieces. Complete vessels may be prepared up to 5000 litres capacity, but they are very sensitive to slight variations in temperature and are also expensive. *Acid-resistant tanks* can be constructed in the factory if a good bricklayer is available: an iron pot is covered with a layer of cement, and when this is dry a layer of acid-proof bricks, or glazed stoneware plates, is fixed to it by means of ordinary cement. The individual plates must be set 6 mms. apart from one another; the resultant grooves are filled up with acid-proof cement, which is obtainable in excellent quality from various firms. The grooves are first half-filled with the aid of a thin wooden spatula, and the cement is dried by heating the whole apparatus with a steam coil, which takes about 14 days. Only when the first layer of the acid-proof cement is quite dry are the grooves completely filled up and again dried. The complete preparation of such a tank holding 5000 litres takes about 2 months. When the cement has set, the vessel is filled with 2 % sulphuric acid and allowed to stand for three days. By this means the acid-proof cement is hardened, and there is no danger of the grooves developing leaks. When properly prepared, such a vessel will withstand even hot 80 % sulphuric acid, and can be guaranteed to stand pressure and vacuum. Vessels are also made with two layers of acid-proof tiles in which the grooves are so arranged that the first set of grooves are covered by the second tiles. They are, however, very expensive, and last hardly any longer than a tank with a single layer when properly made.

Alkaline and neutral liquids may be kept in cement reservoirs which are frequently reinforced with iron. As enormous tensions are developed on heating, the reinforcing must be carefully calculated. Cement vats are also used for the manufacture of colours, but it is advisable to line such vats also with acid-proof tiles as even quite weak acids rapidly corrode the cement. Cement stirrers can also be made and are very useful in special cases.

The floors of works sheds may be covered with a layer of acid-proof tiles cemented together with sulphur; this adheres firmly to the tiles and is not, like asphalt, washed away by hot water. In sheds where the floor keeps dry a good cement surface is sufficient.

Glass, owing to its brittleness, is used relatively little, but often there is no alternative. For chlorinations at high temperatures, for instance, it is indispensable (see also Dichlorbenzaldehyde). Tubing for conveying chlorine is often of glass, and glass stirrers are met with fairly frequently which are made by fixing stout glass rods into an iron or wooden beam. *Fused quartz* is little used as yet, but quartz lamps are coming into favour for chlorinations (*cf*. p. 93).

Porcelain is only found in laboratories and dye-houses. The much vaunted resistance glass vessels burst too frequently to be worth recommending.

Enamel is a particular form of glass which is specially used for coating cast iron. The production of a good acid-proof enamel is no easy matter, and for works plant a double coating is often applied. This enamel has not so good an appearance as the enamel used on ordinary household articles, but it is much more durable. An enamelled apparatus which has developed a defect at any point must practically always be dismantled, for which reason it needs to be treated with great care. Enamelled vessels must never be touched with metal instruments but only with wooden implements. Very complicated pieces of enamelled apparatus are made, which are charged for according to their weight and are very expensive. Enamelled ladles and pots are also much used.

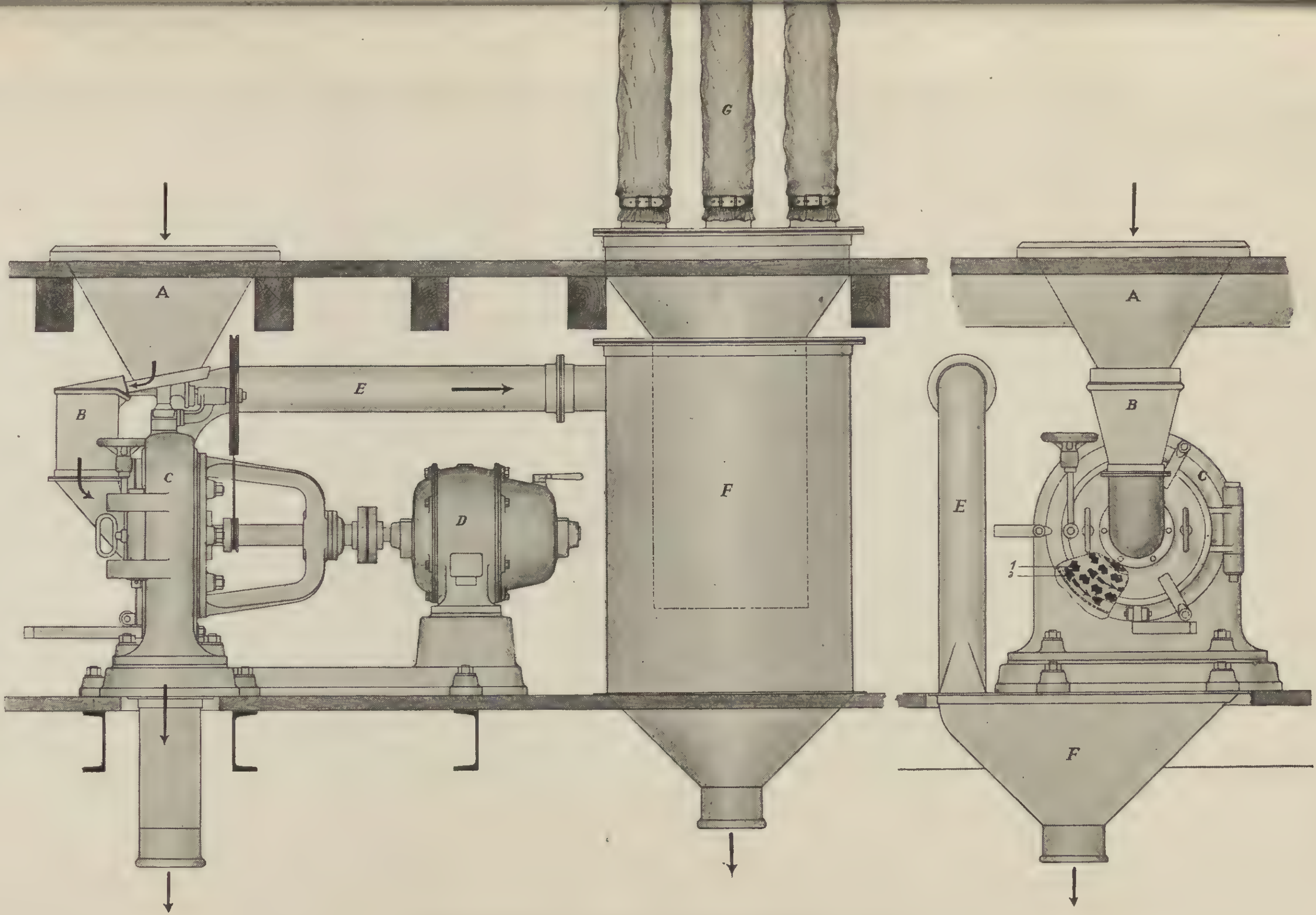
3. *Structural Materials of Organic Origin.*

The most important material of natural origin is, of course, *wood*. It is used for the vats employed in the manufacture of colours, for agitators, scaffolding, and, above all, for the construction of the sheds themselves. In recent years the place of wooden buildings has begun to be taken by reinforced concrete, but it remains to be seen how this lasts. Wood is surprisingly resistant to all chemicals, as it is only attacked on the surface, and this damaged layer serves to protect the material beneath.

In the first place comes American pitch-pine, together with larch and pinewood. Beech cannot be used owing to the large cracks, but oak vats are often found, which are expensive but very resistant. Other woods, with the exception of ash, are not used owing to their high price.

Vats are made of capacities of 20,000 litres ; the stirrers are made of ash and are fixed to the stirring gear by means of wrought iron collars (see also under cast iron). Vats of these dimensions are seldom placed on a platform, as shown on Plate VII, but are usually

PLATE XVII.



Disintegrator for Colours (scale 1 : 20).

Fig. 42.—A. Charging hopper. B. Vibrating device for admitting charge, fitted with magnetic separator. C. Disintegrator. D. Motor. E. Dust conduit. F. Dust chest. G. Dust filters.

stood directly on the ground. The pressure boiler is either sunk in the ground or else is stood by its side, and the liquid sucked out by vacuum.

If a tub is to be evacuated it must be strengthened internally with a cross-beam ; further, to prevent it from flying to pieces on applying a pressure of 2–3 atmos. it must be strengthened by means of strong iron bars. In addition to the syphon tube, a small air tube is also fitted so that the suspensions of the precipitated dye may be kept stirred up by means of compressed air. If this precaution is not observed it may happen that a large portion of the colour remains at the bottom of the tub. All iron bands must be carefully painted with red lead, and often the whole vat is covered with it. If the liquid in the tub is to be heated to boiling it must be covered in to prevent the steam from escaping and as a precaution against accidents ; a proper steam waste-pipe is also necessary, as shown clearly on Plate VII. Steam flues are provided with an air or steam tube with which a powerful draught can be created.

The chambers and frames of filter-presses are made of wood, and where alkaline liquids are to be dealt with larch, or, better, oak, is used in place of the resinous pitch-pine. For filter-press taps small pear-wood faucets are made use of.

Leather is used for driving bands, for the leather collars of hydraulic presses and other less important purposes.

Rubber is the most important of the artificial organic materials. It is used in many forms, such as tubing, as hard rubber for covering centrifuges, ladles, and taps. The rubber coatings of centrifuges last very well, but are rarely used in dye chemistry. Gallic acid is " whizzed " in them, but copper baskets, and even baskets coated with lead by Schoop's process, can often be used.

Manufactured organic substances are represented by *filter cloths*, which are made from *cotton*, *jute*, *hemp*, and *wool*. Filter-press cloths are usually made of cotton, wool being rarely used. Strongly acid precipitates are pressed in camel-hair cloths ; for some time cloths made from Chinese pig-tails were in use, which exceed all others for durability. The so-called *nitro-filters* are much used as filter-cloths, but not in filter-presses, as they have only a very moderate degree of mechanical strength. These are always prepared from a special type of filter-cloth, and since the cotton shrinks on nitration the warp and woof must be of equal strength. Acid-resistant filters can be made only in the following manner : the dry, crude cotton filter is lightly stretched on an aluminium frame, and is dipped into 85–88 % nitric acid at 15–20° ; it is then left in 66° Bé. sulphuric acid for 20 minutes, after which it is thoroughly washed. Such filters can stand the action even of 60 % sulphuric acid at 100°, but they are at once destroyed by acid solutions of ferrous salts.

14. TECHNICAL NOTES ON WORKS MANAGEMENT

As compared with other industries, the value of the entire world-production of dyes is very slight, its worth in 1913, £20,000,000, not equalling a tenth part of the value of the wool crop, nor a fifth of the cotton crop, nor a third of the rubber crop. The dyes are, however, produced under very severe competition, and the finished products fetch a very high price. The energy, intelligence, and perseverance required for their manufacture are without parallel in any other industry.

The development of the dye industry has brought it about that many once carefully guarded secrets are now matters of general knowledge. Ullmann's great "Enzyklopædie der Technischen Chemie" has shown that many processes have long been known to most of the factories. Again, the migration of various workmen has made it inevitable that every important improvement becomes known to competitors in a relatively short time. The success of the great dye factories, therefore, is not founded on any secret processes, but upon the traditions of many years, upon excellent organization, and on the specialities which are protected by patents.

It is a great mistake to think that a colour works can be kept going indefinitely upon specialities alone, and not only do young inexperienced chemists fall into this error, but technical experts and business men frequently express this opinion. Specialities are, so to speak, the choice blooms in the garden of ordinary products, and it is necessary to prepare these commoner, everyday products side by side with the more profitable specialities. In order that a dye factory may be carried on on a big scale it is essential that the standard products should be made in the largest possible quantities. Such mass products or staple products are, first of all, black dyes such as Direct Deep Black EW, Chrome Blacks of various compositions such as Diamond Black PV, Alizarin Black, Erio Chrome Black T, etc.

Next in importance to the black dyes, which constitute over 50 % of the total, come the blue colouring matters, chiefly Indigo, Indanthrene, Direct Blue, and Sulphur Blue. After that come the red dyes such as Alizarin and Benzo Fast Scarlet; and finally, yellow products such as Chrysophenine and Naphthamine Yellow NN.

On the one hand these standard products give the salesman the opportunity of bringing his specialities to the notice of his customers, and, on the other hand, they tend to reduce the general overhead charges to a minimum. Emphasis has been laid already upon the importance of recovering all the by-products produced in the manufacture of intermediates, and it will be unnecessary to add more than a few words.

The various colour factories, recognizing this fact, have united together to form a so-called "Interessengemeinschaft,"[1] the members of which sell their most important intermediate products to each other at the actual cost price, and, in addition, exchange information as to the methods of production. Owing to this concentration of effort it is possible to prepare each intermediate product on a very large scale, and to recover all by-products such as nitrous and sulphurous acids, hydrogen sulphide, thiosulphate, and Glauber salt, in the most rational way. As a necessary consequence of this it will be seen that such a community of interests must also manufacture their own inorganic intermediates in order that they may be independent as regards their supplies of caustic soda, sulphuric and hydrochloric acids, sodium carbonate and chlorine, and also common salt and coal if possible.

The plant used in a colour factory must be up-to-date, and the greatest mistake committed, which is indeed only too common, consists in continuing the use of badly working, out-of-date apparatus. It is often necessary to alter a plant at a day's notice in order to undertake some new manufacture, and it is the business of the superintendent to provide as suitable an apparatus as possible. It is far better to effect once and for all a complete and fundamental reconstruction of the plant than to use an unsatisfactory appliance which takes up a lot of room and requires many workmen to run it. It is nearly always found that in the long run a ruthless, even though costly, alteration is really the cheapest. The calculations are worked out by the Costing Department, which obtains the requisite data from the engineer and from the works chemist. In order that so complex a business as a dye factory shall run smoothly, it requires very careful organization. The actual management is always in the hands both of business men and chemists, who divide up matters between them into various departments, but who are always in direct contact upon all important questions. The commercial director deals with the purchase and sale of products, whilst the chemical directorate is responsible for running the works, the research laboratories and the dye-house. The so-called " Propaganda Dye-house " occupies a more or less intermediate position, and deals with such current business as advertising, the examination of new colours, whether of their own manufacture or made by competing firms, the preparation of pattern cards, and so on. The position of a chemist in a dye factory varies, therefore, very considerably according to whether he is engaged in the dye-house, in the research laboratories, in the works, in the patent department, and so on. The business of the research chemist consists in working out new scientific problems, keeping a careful eye on the technical literature. Too much emphasis cannot be laid upon the fact that it is quite useless to rush into the investigation of a problem until all the available information on the subject has been carefully examined. For this reason well-managed colour factories have a special department dealing with the literature of the subject which is able on request to furnish all details required from its carefully compiled indexes, thus making it possible to obtain quickly a complete summary of the existing information. It is frequently necessary to extend a given reaction over a wide field, and possibly to make hundreds of different dyes and preparations, as it is usually found that only quite a few of the compounds sought have any value (*cf.* Ehrlich-Hata " 606 "). If the Directorate, after consulting with the various departments, such as the dye-house, pharmaceutical laboratory, or other sections, finds a new compound or process of sufficient interest, it is usually put through on a somewhat larger scale. This is carried out in the so-called *Small-scale Plant*, which is an intermediate link between the laboratory and the works. In this technical laboratory is found apparatus which is larger than that used in the research laboratories, but is, of course, far smaller than the actual works plant. In this way it is possible to get an idea as to how the reaction is likely to go on the large scale, thus frequently saving large sums of money.

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[1] Literally="Community of Interest," and is commonly referred to as the "I.G."

Further, at this stage it is decided whether a reaction or a compound shall be patented. It is the task of the patent department to decide as to the likelihood of obtaining a patent or whether, if the discovery appears to be important, it would be preferable to keep it secret until the whole field has been investigated, and there is little danger of any one else trespassing. Very occasionally patent protection is not sought, and the attempt is made to keep the processes secret, but this is by no means a safe proceeding, and is only resorted to in cases of necessity.

The chemists are required to submit a report on their activities to the Directorate at regular intervals in order that the Directors and heads of departments may be kept in touch with all developments. These reports are submitted monthly, or at less frequent, but regular, intervals, and are drawn up under the supervision of the departmental heads.

Before a product is put on to the works to be manufactured it is first sent to the Costing Department to be costed. The necessary data are provided by the chemical administrative staff and the works engineer. In Chapter 15 a small calculation is shown as an example, in order to give a general idea of the manner in which the cost-price of a dye is arrived at.

Management.—The actual Management is divided into three sections, the Technical Chemical Department, the Analytical and Dyeing Department, and the Engineering Department.

Owing to the destructive action of the chemicals used, apparatus is very quickly worn out and, in addition, alterations are frequently necessary, so that the ratio of the number of chemical workers to that of the ordinary workmen (*e.g.* locksmiths, pipe-fitters, carpenters, painters, bricklayers, etc.) is about 2:1. The workshops are first of all repairing shops, and are under the direction of the works engineer. If any repair or alteration is required to an existing plant, the works chemist, with the sanction of the management if it is a large matter, applies to the engineer. The work is ordered by means of a special form duly filled in, which, on completion of the job, is sent to the Costing Department to be worked out.

The large dye factories have their own constructional workshops, but nevertheless place their large orders outside after making a suitable agreement with some engineering works for quick delivery at reasonable rates. It is advisable not to use too many types of plant so that any part or agitator may be replaced at once from stock. Frequently quite a few spares suffice for many different plants, as they are mutually interchangeable.

Charges.—In addition to the charges due to depreciation and repairs, there are maintenance charges of various kinds to be considered. Some of these are calculated exactly, whilst others are lumped together as general overhead charges or "On-costs." The expenses which can be estimated fairly accurately are workmen's wages, which can be calculated from the wage-sheets of the foremen and works chemists; further, the steam consumption can be measured with the usual type of steam meter, and also the amount of compressed air and vacuum used.

Steam Consumption.—The steam consumption of a colour factory is considerable, and depends upon the amount of water which requires to be heated and on the number of cubic metres of water which have to be evaporated. In particular, the evaporation of reduction liquors demands immense quantities, and multiple-effect evaporators (double and triple effect) are being increasingly used. In this type of apparatus the heat of the steam is used two or three times over by leading the waste steam into a second boiler, where it evaporates a further quantity of liquid kept under reduced pressure. This apparatus is modelled partly upon the multiple-effect evaporators used in the beet-sugar industry, and in some cases they possess heating vessels which are placed next to the reservoir of liqud. The liquid is made to circulate through the tube evaporator, thus attaining a rapid circulation, and in addition the boiler-scale (chiefly gypsum) is deposited solely in the subsidiary vessel, the tubes of which can be replaced in a few hours. It is possible by this regenerative utilization of the steam to reduce the coal consumption to less than 25 %, so that the large dye-works use triple-effect evaporators almost exclusively with very satisfactory results. It is possible to utilize the steam still more efficiently by heating it up to 15 atmospheres instead of the usual working pressure of 5 atmos. Before this high-pressure steam reaches the works it is used to drive a steam turbine or a reciprocating engine, leaving this at 5 atmos. pressure. So much energy is obtainable from the pressure drop of 15–5 atmos. that each dye works can actually provide surplus electric current. It has also been suggested that the steam should be allowed to fall as low as 2 atmos., but in order to do this the steam pipes must be so large and the radiation losses, particularly in winter, so considerable, that it is hardly practical politics. Of recent years an improved method for using up steam has been introduced, although the general principle has been known for a long time. The liquid under evaporation is placed in an hermetically closed evaporator, the vapours are sucked out by means of a turbo-blower, and the waste steam is then circulated, under a pressure of about $\frac{3}{4}$ atmos. through a system of tubes built into the same vessel. There is a considerable evolution of heat as a result of the compression of the vapours, so that as much as 80 % of fuel may be saved. Apparatus of this type is becoming increasingly popular, and is made, for example, by Gebr. Sulzer in Winterthur, and by Escher Wyss in Zurich.

Compressed Air and Vacuum.—In addition to steam, the

PLATE XVIII.

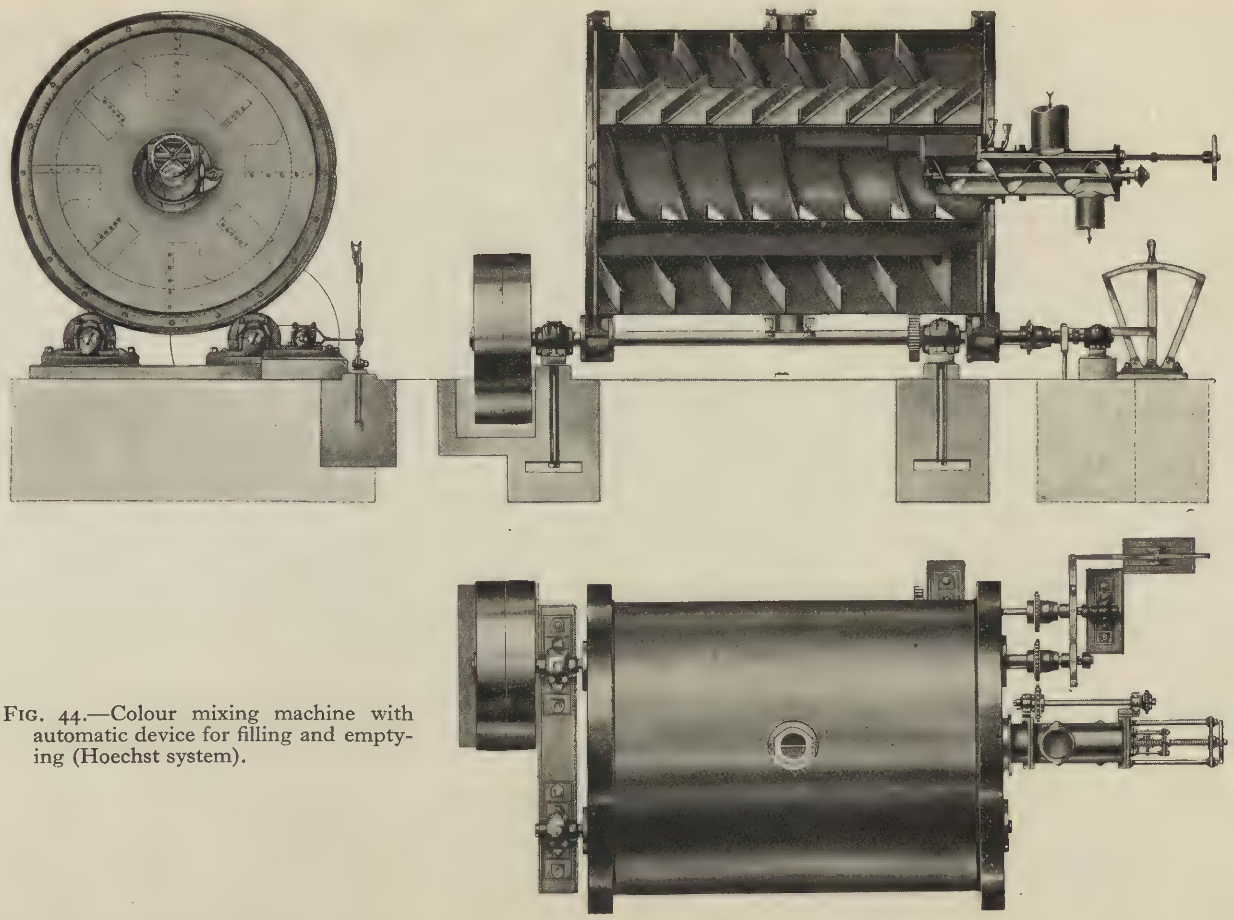

Fig. 44.—Colour mixing machine with automatic device for filling and emptying (Hoechst system).

provision of compressed air is also important. Generally a pressure of 2–3 atmos. is needed, which is obtained by the use either of a reciprocating or a rotating pump. The chief determining factor as to the quantity of air required is the number of filter-presses, as these use the most air. Every precipitate before leaving the press is " blown through " for a time, *i.e.* compressed air is blown through the filter-cakes until the main portion of the mother-liquor has been blown out. For instance, a press with 40 sections will require about 100 cubic metres per hour of compressed air at 2 atmos., which will cost from 3–5 centimes, according to the price of the current.

The provision of air for a dye works is therefore a considerable item of expenditure, and must be carefully estimated. A very satisfactory type of compressor and vacuum pump is that shown on Plate XVI, made by the Schweiz Lokomotiv und Maschinenfabrik in Winterthur (Witte's system, *cf.* also, p. 189).

The cost of the water used must also be carefully determined by the engineer by accurate measurement, as very large quantities of water are employed, particularly as cooling water for the condensers.

Duties of the Works Chemist.—The work of the supervising chemist is possibly the most interesting in the whole of the industry, as it is impossible to control chemical reactions merely by giving an order, but their course must be accurately followed the whole time and any deviations corrected. The chemist must be *au courant* with the whole process, and must know every stage of the manufacture in full detail. In this connection attention may be called to the remarks made on Benzo Fast Blue (pp. 144–5).

Manufacture.—The ordering of the necessary raw products is done by means of requisition forms which are usually sent to the Material Stores on the previous day, or occasionally to some other department of the works. The chemicals are brought to the shed on the evening before they are required so that everything will be ready when the manufacture is begun. The chemist is responsible for the products until the moment that they issue in the dry form from the shed. As many colours are sensitive to heat, and therefore require careful heating, their drying must always be supervised by the chemist so that he will always be able to give an account of the effect of the drying upon the strength and shade of a dye. Such cases have been dealt with in connection with Methylene Green and Azo Yellow.

Standard Dye-House.—The finished colour is sent directly from the drying shed to the dye-house, where a small sample is dyed out against the *Type or Standard*. The figures obtained are sent immediately to the management, the costing department, and the chemist concerned in the matter, so that all may be kept continuously informed. Frequently a dyeing test is carried out with a small sample of the colour taken directly from the filter-press, so that any faults may be recognized at that stage.

Drying.—In recent years vacuum drying chests have been coming more and more into use, as it has been shown that the steam consumption is less and the strength of the product greater. Plate XVI shows a modern vacuum dryer as used with various modifications. Stable intermediate products such as sodium β-naphthalene sulphonate, and simple azo colours, can be dried simply on steam plates, or may even be dehydrated in tunnel-kilns on the counter current system, though here also vacuum drying is becoming more general owing to the saving both of time and space. The Badische Anilin- und Sodafabrik, for instance, make use of about 500 vacuum dryers, and have, so far as possible, given up the older system of drying.

In order to dry a product rapidly it must be ground up at least once during the drying. As much dust is formed during this breaking up of the press-cake, many drying sheds are provided with dust extractors.

A modern improvement is to condense the vapours from the drying chests so that the pumps do not suffer so much from the action of acid or alkaline vapours.

Standardization.—When a certain number of works batches have been dried, they are ground up and made up to a standard or type strength. The grinding and mixing is usually carried out in a special mixing department which is under the control of the dye-house. (This dye-house has no connection with the scientific and commercial propaganda dye-house, which is intended to serve quite another purpose.)

Grinding.—Nowadays the colours are ground up in modern centrifugal mills, such as that shown diagrammatically on Plate XVII. The capacity of such a machine exceeds that of the older edge-runner mill or ball-mill by some 10–50 times, whilst at the same time the particles are ground smaller. Many complaints of inadequate solubility of a product are to be ascribed to incorrect grinding, as, in the older types of apparatus, the substances were pressed together, thus producing almost shaly tablets of great hardness which dissolve only with difficulty.

Whenever possible the approximate necessary quantity of diluent is ground up with the dye so as to diminish the length of time necessary for the mixing. The concentrated colour is mixed with the standardizing material (Glauber salt, common salt, soda, or dextrin), and the mixture is run into the mill. The disintegrator illustrated has an automatic sieve and also magnets for the removal of iron particles, which are always present in the materials. The dye is broken up whilst in motion by the specially shaped grinding pins, and is whirled round and round until it passes through the sieve (Fig. 39). Owing to the centrifugal effect, much air is sucked in,

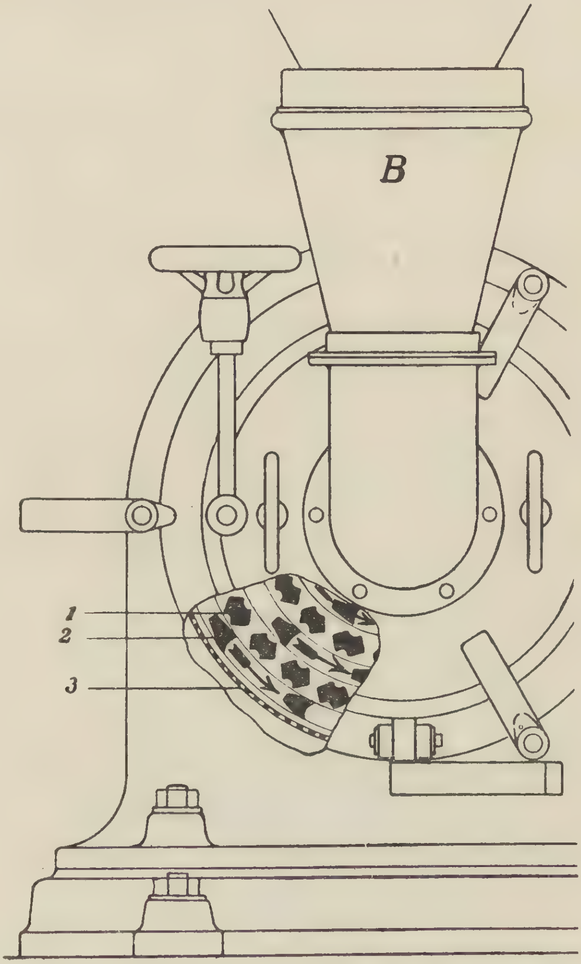

FIG. 39.—Diagram of a "Perplex" disintegrator.

B. Feed-pipe. 1. Fixed grinding pins. 2. Rotating pins (1200–2000 rotations per minute). 3. Sieve.

which must be allowed to pass out from the apparatus again. Filter-bags (G, Plate XVII) in the form of piping permit the escape of the air, but keep back all the dust. The main portion of the powder is retained in the air chamber (F), the stream of air striking the walls tangentially. If very soft material is being disintegrated, such as β-naphthol or naphthalene, it is better not to have the sieve as it is readily stopped up. The ground products are carried by means of worm-conveyors direct into the mixing troughs, where they are well mixed up for several hours. Plate XVII (Fig. 42) shows a modern mixer which can be filled or emptied automatically by means of a reversible worm-feed. This type of mixing apparatus is made for dealing with quantities up to 4 tons, and is gradually replacing the older, uneconomical mixers, particularly when very large quantities are being dealt with. Simpler mixers are also made use of which are provided with compressed air and vacuum, like grain-silos. Certain dyes must be pulverized outside the grinding shed owing either to a danger of fire (picramic acid dyes) or owing to their unpleasant properties (*e.g.* Bengal Blue or Naphthol Blue, p. 173). As soon as the strength and shade has been passed by the dye-house as correct, the dye is sent off to the packing-house, from whence it is handed over to the Sales Department. The management, costing department, and works chemist are all informed of any matters of special interest such as good or bad yields or shades. The responsibility of the works chemist finishes with the delivery of his products whether dyes or intermediates.

15. EXAMPLE OF THE COSTING OF A SIMPLE DYE[1]

Orange II = Acid Orange A.

(Sulphanilic Acid—β-Naphthol ; see p. 113.)

The costing of the product of the dye factory is always done by the Costing Department. This department obtains daily, weekly, or monthly, the necessary data from the various manufacturing departments, from which the prices may be calculated with very great accuracy. The position of head of the Costing Department is a very responsible one, and, next to the actual management, he is the most important person in a modern colour factory.

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[1] The prices and charges used in this calculation represent average figures for 1913-14. The example is intended simply to show the beginner how the final cost of a relatively simple Azo dye is made up from numerous separate items.

The cost of a product is made up solely from the *cost of materials* and the *workmen's wages.*

Every item which is to be added to the price of a product must be based upon very carefully scrutinized figures.

We will first determine the cost of the separate components.

β-Naphthol.[1]

	Fr.
260 kgs. Naphthalene at 11 frs. per 100 kilos.	28·60
280 kgs. Sulphuric acid at 2·70 frs. per 100 kilos.	7·56
60 kgs. Soda at 9 frs. per 100 kilos.	5·40
60 kgs. Coal at 2 frs. per 100 kilos.	1·20
350 kgs. Salt at 1·40 frs. per 100 kilos.	4·90
Yield of β-naphthalene sulphonate 165 % = 429 kgs. =	47·66
∴ 100 kgs. cost 11·10 frs.	

This price is known as the "*First Price,*" or "*A price.*" It contains only the cost of the materials purchased or obtained from other departments (for instance, sulphuric acid from the acid factory, etc.).

There are a number of other charges to be added to this First Price, which are made up from items such as wages, repair, or wear and tear of apparatus, cloths for pressing filter-cakes, drying of the sulphonate, cost of carriage, grinding, power, steam, and water. All these figures must be very accurately determined if a correct idea of the whole process is to be obtained. It is hardly necessary to add that these calculations can only be carried out by a carefully trained staff. The calculation of the workmen's wages is based upon the time-sheets, which are controlled and examined by the superintendent.

The works chemist should be concerned as little as possible with administrative duties of this kind as they merely keep him from his real business, namely, chemistry. He should keep an eye, however, upon the works log book and the chemical log book at least each week, the resultant figures only going to the Costing Department when he has passed them.

In a similar manner the other charges are obtained from those in charge of the stores and the repairing shops, and from the data furnished by the works engineer. It is usual to carry out tests from time to time, by actual measurements, of the steam and water requirements for a given product.

These charges may be spread over the different products in various ways. For the sake of simplicity we will assume that the charges are in respect of 100 kilos. of dried product, and that it has been determined that the various charges for the dry β-naphthalene sodium sulphonate are calculated as follows :—

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[1] Based on the assumption that the factory is in a country producing its own coal.

	Fr.
Wages, 2 hours at 0·80 frs. per 100 kilos. (including insurance, welfare, etc.)	1·60
Power, 4 k.w.-hours at 4 centimes per k.w.-hour (pressing and stirring, including compressed air)	0·16
Drying and grinding at 20 centimes per 100 kgs. (tunnel-kiln drying)	0·20[1]
Total charges for producing 100 kilos. sodium-β-naphthalene sulphonate	1·96
100 kilos. (first cost)	11·10
	13·06

Alkali Melt of Sodium Salt.

In actual practice large amounts (from 400 to 2000 kilos. of the sodium salt) are melted, but to simplify the calculation we will assume that we are dealing with a charge of only 100 kilos.

	Fr.
100 kgs. "Naphthalene salt"	13·06
45 kgs. NaOH at 17 frs. per 100 kilos.	7·65
15 kgs. Coal at 2 frs. per 100 kilos.	0·30
20 kgs. Sulphuric acid at 2·70 frs.	0·54
Labour for melting, dissolving, and distilling	5·00
Fuel for melt and distillation, condensing water, and compressed air	2·00
Interest (5 frs. per 100 kilos., yield 45 kgs.)	2·25
Total	30·80
Less value of recovered sulphite and Glauber salt	2·00
Cost of production of 45 kilos. pure Naphthol	28·80

1 kilogram pure naphthol, therefore, costs 64 centimes.

In addition there are the general "on-costs" which may be reckoned at about 5 %, so that the final cost price of the beta-Naphthol is about

67 centimes per kilogram.

In Switzerland it is, of course, quite impossible to get such low figures, as coal and other raw materials are far more expensive, so that allowance must be made for at least double the above figure.

Actually, before the war, β-naphthol was obtainable in Switzerland in barrels, at a price of about 95 centimes per kilo., including packing, freight, and duty. It may be seen, therefore, that at best only about 10 centimes profit could be made per kilo. We can therefore put our naphthol at about 95 cts., with the proviso that the large German works had a lower cost-price as they were able either to make large contracts on favourable terms or to manufacture the naphthol themselves. In any case the manufacture shows so little profit that the majority of factories prefer to purchase their naphthol from the large works who do make it, and to concern themselves with more profitable products.

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[1] The drying is effected by means of the waste heat from the fusion pot.

Sulphanilic Acid.

(a) *Nitrobenzene :*

	Fr.
100 kgs. Benzene at 32 cts.	32·00
110 kgs. HNO_3 (75 %) at 40 cts.	44·00
170 kgs. K_2SO_4 2·70 frs.	4·60
	80·60
Yield : 154 kgs.	
Repairs and depreciation, 50 cts. per 100 kgs.	0·77
Labour, at 35 cts. per 100 kgs.	0·54
Total for 154 kgs. Nitrobenzene	81·91
Less 3 frs. for recovered spent acid	78·91

Cost of 1 kilo. Nitrobenzene about 55 centimes.

Actually the larger works can produce it more cheaply, at less than 50 centimes.

(b) *Reduction of Nitrobenzene :*

We will assume that exactly the 154 kgs. are reduced, remembering, however, that in actual practice charges up to 2000 kgs. are dealt with.

	Fr.
Nitrobenzene, 154 kgs. about	85·00
Iron, 40 kgs. at 3 cts.	1·20
Hydrochloric acid, 4 kgs. at 4 cts.	0·16
Lime, 4 kgs. at 1·25 frs. per 100 kgs.	0·05
Steam, repairs, depreciation, distillation, power, etc., for 154 kgs. Nitrobenzene	5·00
Total	91·41

Yield 110 kgs. Price per kilo. 83·1 centimes.

If it is remembered that the price of aniline has at times gone down as low as 85 cts. per kilo. in the open market, it is not difficult to realize that practically no profit could have been obtained on it, and the suggestion sometimes made by purchasers that too high prices were charged for it is seen to be without foundation. At the same time it is certain that the large aniline works, such as Weiler-ter-Meer and others, had considerably lower production costs.

	Fr.
110 kgs. Sulphuric acid at 2·70 frs.	2·97
93 kgs. Aniline at 1 fr. per kg. (price in Switzerland)	93·00
	95·97
Labour, 5 hours at 80 cts.	4·00
Steam (baking-stove) coal	2·50
Upkeep at 10 cts. per 100 kgs.	0·17
Total	102·64

Yield about 163 kgs. 100 % Sulphanilic acid.
Price about 70 cts. per kilo.

We have now determined approximately the prices of the intermediate products, but these will, of course, vary according to circumstances and serve chiefly to show how difficult it is to get really accurate figures.

We will assume that the Sulphanilic acid costs us 70 cts., and the β-naphthol 95 cts. per kilo., according to the usual conditions obtaining in Switzerland.

Preparation of the Dye from Sulphanilic Acid and β-Naphthol.

We will take the kilogram-molecule for our unit, and for this purpose we multiply up the Acid Orange charge given on p. 113 by 10,000.

	Fr.
173 kgs. Sulphanilic acid at 70 cts. per kg.	121·10
60 kgs. Sodium carbonate at 7 cts. (Swiss price, 10 cts.)	4·20
144 kgs. β-Naphthol at 95 cts. per kg.	136·80
144 kgs. Caustic soda lye (30° Bé.) at 6 frs. per 100 kg.	8·64
110 kgs. Sulphuric acid at 2·70 frs. (Swiss 4·0)	2·97
70 kgs. Sodium nitrite at 51 frs. per 100 kg.	35·70
250 kgs. Sodium carbonate at 7 cts. per kg.	17·50
800 kgs. Ice at 80 cts. per 100 kgs.	6·40
200 kgs. Salt at 1·40 frs. (Swiss, about 3·50)	2·80
Total	336·11

Yield about 400 *kgs.* concentrated product; containing salt and soda as impurities.

	Fr.
Labour, 12 hours at 80 cts.	9·60
Running expenses based on dry concentrated product, per 100 kgs.:—	
Drying 400 kgs. at 8 frs. per 100 kgs.	32·00
Mixing and grinding, at 4 frs. per 100 kgs.	16·00
Air, steam, water, power, at 4 frs. per 100 kgs.	16·00
Total	73·60

The dye-house expenses are either charged up to the process or to the general account. In the opinion of the author only the expenses of the standardizing dye-house should be included, the cost of the upkeep of the " propaganda " dye-house being allocated to the general propaganda and advertising account. These latter expenses are much larger than those for the standardizing dye-house, and logically they should be kept as separate items.

We include here, therefore, only the manufacturing charges, which we may estimate at about 1·80 francs per 100 kgs. of finished product, which equals 7·20 frs. :

	Fr.
Dye-house charges	7·20
Other charges	73·60
Total of " On costs," excluding general works expenses	80·80
Total first costs of Acid Orange A, excluding general works charges, for 400 kgs.	336·11
Total	416·91

In addition there must be added certain other charges, usually termed general works expenses, which are made up from the following items : railway, cleaners, etc., stores, care of the factory (porter, night-watchman, etc.). The costs of the analytical and works laboratories are also included, but not the salaries of the research chemists.

This figure may vary very considerably according to the amount of the turnover. Usually these general expenses may be estimated at about 5–7 % of the value of the finished dye. Occasionally with products which are meeting with keen competition, smaller expenses will be charged up to them, but such matters are, of course, essentially for the Sales Department, and are decided by the managerial staff.

In the present case, therefore, we may assume that a figure of 6 % may be taken to cover these general on-costs, 6 % of 416·91 frs. = 25·02 frs., so that the actual *cost price of the pure product is* 441·93 frs. *per* 400 *kilos.*, or about 1·10 *franc per kilo.* This product is then reduced to standard strength by means of salt as mentioned on p. 216.

IV. ANALYTICAL SECTION

16. ANALYTICAL DETAILS

The exact determination of the composition and degree of purity of the raw and intermediate materials used for the production of dyes is of the greatest importance. The methods in use are partly physical and partly chemical. In many cases it suffices to obtain certain physical data such as Melting Point, Solidifying Point, and Boiling Point; aniline, the toluidines, nitro compounds, etc., are usually tested in this way. Sometimes the Specific Gravity (Density) is determined in addition, and occasionally also the Refractive Index for monochromatic light. Practically all the important details are given in Lunge's work on "Coal Tar and Ammonia." The properties required are often specified in the contract, and serve as standard to work by in case of any differences being detected.

At the present day intermediates are placed on the market in such a pure form that all reasonable requirements can be fulfilled.

Samples of materials which it is proposed to purchase should in all cases be tested in the Analytical Laboratory; the method of sampling is frequently specified in the contract. Even the method of heating to be adopted when determining the melting or solidifying points is usually standardized. In the works the practice is sometimes adopted of determining the strength of the technical solutions in use, the actual yield being only estimated at the end of the process. In the larger factories, however, it is becoming increasingly the custom to weigh all solutions at once in their barrels, scales being used which can weigh up to 40,000 kgs. with a sensitiveness of 100 gms.

Each product used in the dye industry is characterized by its *Molecular Weight*, which is calculated simply from its chemical formula. Owing to the fact that various substances are used in different forms, *e.g.* benzidine as sulphate and as base, Cleve acid as free acid and as the sodium salt, it is customary to give one molecular weight to each given substance, the salt being reckoned as of a correspondingly lower degree of purity. When purchasing materials, therefore, it is necessary to ascertain the molecular weight of the

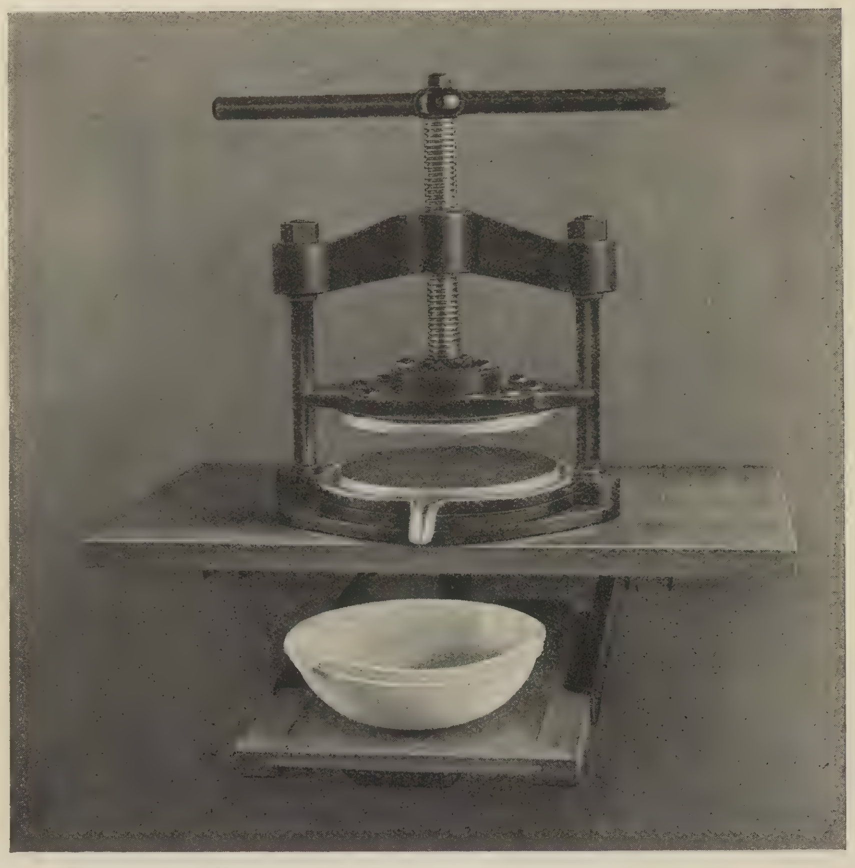

FIG. 45.—Screw press with wrought iron frame (made by Preiswerk and Esser, Basle). The base-plate is covered with copper sheet and the products are pressed between hard-wood boards.

bodies as well as the price per kilo. Suppose, for instance, that 1 kg. benzidine (mol. wt. = 184) costs 3 frs. per kilo., and 1 kg. benzidine sulphate (mol. wt. = 282) 2 frs. per kilo., then the pure base in the sulphate will cost $2 \times 282/184 = 3{\cdot}02$ frs., that is to say, the price is practically identical. This is sometimes expressed by giving the degree of purity as a percentage. In the present case, for instance, the sulphate would be 65·2 % (mol. wt.=184), *i.e.* 184 kgs. benzidine base (mol. wt.=184) will be obtained from 282 kgs. sulphate.

Preparation of Standard.

Sodium nitrite is generally estimated in commerce by oxidation with permanganate in the usual manner, but this gives values which are slightly too high for the works chemist. Besides the nitrous acid the permanganate gives also any other oxidizable substances which may be present, so that, under certain conditions, slight errors may be caused. In spite of this, however, this method is adopted in various factories, such as the Notodden nitrite works. For the colour chemist, however, there is only one really dependable method, namely, the *Sulphanilic Acid Method*, which is fully as accurate with a little practice and is safer.

Preparation of pure Sulphanilic Acid.

250 Gms. of commercial sulphanilic acid are dissolved in sufficient sodium carbonate to give a strongly alkaline solution, which is boiled until all aniline has disappeared. The volume is about 1 litre. The solution is now filtered and made strongly acid by means of hydrochloric acid. After standing 12 hours the product is filtered off, washed with a little water, and the crystals dissolved to a neutral solution in 400 c.cs. water and a sufficient quantity of soda (about 60 gms.) The hot solution is cooled down to 0° with continuous stirring and the sodium sulphanilate is filtered off. If a small centrifuge is available, the mother-liquor is " whizzed " off. The crystals are dissolved in 500 c.cs. of distilled water, the solution filtered, and then acidified with pure concentrated hydrochloric acid. The liquid is kept well stirred during the addition in order to ensure the formation of small crystals ; next day the precipitate is filtered off and is then washed with a little distilled water until the sodium chloride is removed. The purified crystals are again recrystallized from boiling distilled water and are then dried in an air oven at 120° until of constant weight. The product is kept in a bottle having a

well-fitting ground stopper. The sulphanilic acid so obtained is practically white and contains less than 0·01 % of impurities. Exactly 173 gms. are dissolved in 100 c.cs. pure ammonia (20 % NH_3), and it is then made up to 1 litre at 17·5°. Such a solution will remain unchanged in the dark for many months, but should be carefully recontrolled at intervals of 3 months.

This standard solution serves for the preparation of Normal sodium nitrite solution.

Preparation of Normal Nitrite Solution (**N**.$NaNO_2$).

75 Gms. commercial sodium nitrite are dissolved in a little water, filtered, and made up to 1 litre at 17·5°. 50 C.cs. of the normal sulphanilic acid solution are then titrated with it in the following manner:

The solution is measured out into a half-litre beaker by means of a pipette, and is then diluted with 200 c.cs. ice water and acidified with 25 c.cs. crude conc. hydrochloric acid. The nitrite solution is then run in under the surface of the liquid from a burette, and as soon as 45 c.cs. have been added, the remainder is run in drop by drop until the starch-iodide paper when *touched* with a drop of the liquid (not rubbed across) causes a faint but permanent blue coloration. The diazotization occupies 10 minutes. From the number of c.cs. of nitrite solution used up it is easy to calculate how much water must be added to render the solution exactly normal. It is then made up exactly to the requisite strength, as the use of a factor causes too much unnecessary labour. The little extra work involved in standardizing the solution is more than made up by the subsequent saving in time.

When the sulphanilic and nitrite solutions have been made up as described, a *Normal aniline solution* is also prepared: 200 c.cs. pure aniline are distilled from a small distilling flask as shown in Fig. 43[1] at such a rate that the distillation occupies about three-quarters of an hour. The fraction of aniline distilling within half a degree and between 184 and 185° is used for the preparation of the solution. In passing it may be noted that almost chemically pure aniline is obtainable commercially. The specific gravity should be between 1·0260–1·0265 at 17·5°.

Exactly 93 gms. pure aniline are dissolved in 150 c.cs. of pure

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[1] High-boiling liquids are generally distilled with this simple type of apparatus *i.e.* without the use of a Liebig condenser, the receiver being sometimes cooled with a stream of water.

30 % hydrochloric acid, and the solution is made up to 1 litre at 17·5°.

If the sodium nitrite solution and the sulphanilic acid solution have been correctly prepared 100 c.cs. sulphanilic acid solution and 100 c.cs. aniline solution should each require exactly 100 c.cs. nitrite.

Preparation of N/10 Phenyldiazonium solution.

50 C.cs. of aniline solution are measured out, treated with 50 c.cs. concentrated hydrochloric acid, and the mixture cooled by standing the measuring flask in ice water. 50 C.cs. N-nitrite solution are then added to it with gentle shaking, and the whole allowed to stand in ice water for 20 minutes. At the end of this time all the nitrous acid will have been used up except for the merest trace, and the solution is then made up to 500 c.cs. and is ready for use. Not less than 20 minutes must be allowed to elapse before using the solution as the diazotization under these circumstances takes some time. Such a solution will keep in the dark at 0° for about 4 hours, and must always be freshly made for use.

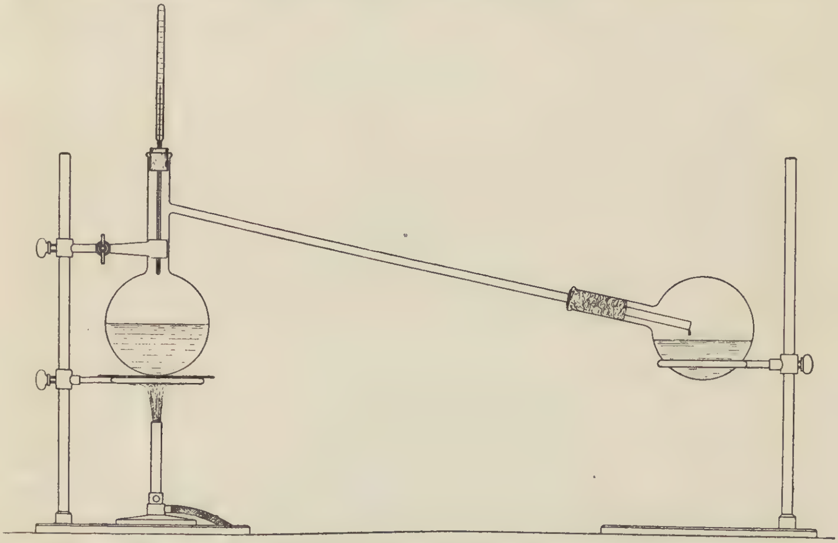

FIG. 43.—Distillation of a liquid of high boiling-point.

Estimation of Amines.

(a) *Direct Estimation.*

The method consists in titrating the amine in very dilute solution with hydrochloric acid and sodium nitrite, the resultant diazonium solution being then coupled up with an exactly determined amount of a phenol, usually Schäffer salt, the diazotization being thus controlled. In the cases of H-acid, Amido-R-salt, etc., one portion is diazotized whilst another sample is coupled up with aniline or other component. Sometimes it is possible to estimate two substances in the presence of one another if one reacts much more rapidly than the other. For instance, with a little practice it is quite possible to estimate G-salt and R-salt side by side with a fair degree of accuracy, as R-salt couples very rapidly and gives a red dye with aniline, whilst G-salt couples afterwards and forms a yellow dye. In addition to these methods there are a number of special methods which make it possible to estimate the various components in a mixture. Such methods have been noticed when discussing mixtures of R- and G-salts (*cf.* p. 233).

Certain other diazo components are used occasionally in place of benzene diazonium chloride; thus, many works prefer to use *m*-xylidine in place of aniline, but there is very little point in so doing, as its solution is less stable than the aniline solution. Again, in some cases *p*-aminoacetanilide is made use of as it couples up rather more energetically and is quite reasonably stable (*vide* Chromotrope acid); ortho- and para-nitranilines are rarely used.

5 Gms. sodium carbonate are required for each gm. nitrite or, if the coupling is carried out in acetic acid solution, at least 15 gms. sodium acetate are added, or twice this amount in the case of the nitranilines. Should the substances contain sulphonic groups, still more sodium carbonate or acetate will be required. The temperature for the coupling should not at any time exceed 5°, and the solution should be very dilute (about 1 %).

The excess of diazonium salt is determined by spotting on filter-paper, easily soluble dyes being first salted out. As a suitable reagent for amines or easily-coupling phenols such as resorcinol, a solution of R-salt or H-acid is used. Some factories make use of a freshly prepared solution of hydrocyanic acid which gives a yellow coloration. The presence of excess of the phenol or amine which is being determined is ascertained by spotting on filter-paper with the diazonium solution. The loss so caused is so small that it may be neglected.

(b) *Indirect Determination.*

In the case of certain amines it is not possible to estimate them by direct diazotization owing either to their forming diazoamino compounds or diazonium salts which blacken starch-iodide paper in the same way as free nitrous acid. Amines of this type, *e.g.* nitranilines, chloranilines, etc., must therefore be estimated indirectly. Thus, 1/100 mol. of the amine in question is dissolved either in concentrated or slightly diluted hydrochloric acid, poured into water and ice and diazotized with a fair excess of sodium nitrite. The clear diazonium solution is poured into a measuring flask, made up to a known volume, and is then run in from a burette or measuring cylinder to a strongly alkaline β-naphthol solution of known strength until, on testing on filter-paper, no naphthol can be detected with diazonium solution on the edge of the spot. Usually the quantities are so chosen that the number of c.cs. used divided into 100 gives the percentage of amine sought for.

Example: 3·45 gms. *p*-nitraniline (=2·5/100 mol.) are dissolved in 10 c.cs. hydrochloric acid of 30 % strength, and 10 c.cs. water. The clear solution is poured on to 50 gms. ice and 50 c.cs. water, and is then treated with a solution of 2 gms. 100 % sodium nitrite in the form of a 20 % solution. Owing to the slight excess of nitrous acid (about 0·2 gm. $NaNO_2$), a clear solution is produced, which is made up to 250 c.cs. in a graduated flask. 100 C.cs. of this solution are measured out into a cylinder, and are then added by degrees with stirring to a solution of 1·44 gms. 100 % β-naphthol dissolved in 2 c.cs. of 30 % NaOH to which 20 gms. sodium carbonate in 300 c.cs. ice water have been added. By means of spotting tests the point is determined at which β-naphthol ceases to be indicated with diazonium solution on the rim of the spot. The number of c.cs. of nitraniline solution used divided into 100 (100/c.cs.) gives the percentage required. If the nitraniline is 100 % pure, then exactly 100 c.cs. will be required. Usually 101–102 c.cs. are needed.

Estimation of Naphthols.

β-Naphthol.

1·42 Gms. (=1/100 mol.) naphthol are dissolved in 2 c.cs. caustic soda-lye of 30 % strength, and 25 c.cs. of 10 % sodium carbonate solution are added. Ice-cold diazobenzene solution is then run in from a measuring cylinder or an ice-jacketed burette until a drop tested on filter-paper no longer forms any orange-red dye on its edge when tested with diazonium solution. Owing to the presence of impurities a coloured line sometimes forms after a few seconds where the paper has been touched, but the colour is always muddy, and with a little practice can always be distinguished from the pure naphthol colour. The number of c.cs. used gives directly the percentage composition of the β-naphthol. A good quality product should be at least 99·5 %.

α-Naphthol.

α-Naphthol couples much more readily than β-naphthol, and would give too high values in alkaline solution. For this reason the coupling is effected in acetic acid solution in the following manner: the α-naphthol is dissolved up in the same way as the β-naphthol, and is then precipitated with dilute acetic acid in presence of 25 c.cs. of 25 % sodium acetate solution. The coupling is then effected as described for β-naphthol, and as soon as the reaction for α-naphthol has disappeared the whole is dissolved up by adding caustic soda solution, after which it is reprecipitated with acetic acid; "aniline solution" is added, and so on until the α-naphthol reaction has really completely gone. Frequently it is necessary to add as much as 30 % of the diazo solution subsequently owing to the naphthol being carried down with the precipitated dye.

Only α-naphthol can be estimated in this manner, as β-naphthol does not couple in acetic acid solution. If it is subsequently desired to estimate the β-naphthol content as well, diazotized nitraniline solution is added until all the β-naphthol has been coupled up. In this way it is possible to estimate both naphthols in an impure specimen of α-naphthol.

Dihydroxynaphthalenes (M.w. 160).

These are determined in the same way as for α-naphthol. They couple up very quickly and the "after-coupling" is usually very pronounced and impure, so that it is easy to determine the end-point.

Aminosulphonic acids.

1/100 Molecule of the acid is dissolved in the requisite amount of sodium carbonate solution, which is then diluted to 250 c.cs., 25 c.cs. concentrated hydrochloric acid are added and the whole titrated with normal Nitrite solution. The number of c.cs. multiplied by 10 gives the percentage composition. Care must be taken only to *spot* the nitrite paper, as it is impossible to get accurate results if the paper be stroked with the rod.

Notice should be taken of the fact that very energetic diazonium salts can themselves turn the starch-iodide paper blue rapidly, and it is also essential to know the relative sensitiveness of the paper.

Sulphanilic acid, metanilic acid, and naphthylamine sulphonic acids are diazotized at 15°.

Cleve acids cannot be determined so easily, as they couple up at once with themselves. In this case it is best to add the greater part of the nitrite to the neutral solution and then to acidify, stirring well. Or the solution may be diazotized directly at 0°, nitrite being added until the violet coloration first produced changes to a pure brown. The indirect nethod is, however, to be preferred. as it is more rapid.

Estimation of Aminonaphthol Sulphonic Acids.

Two different determinations are always made. First of all the amount of nitrite required is measured and this figure is termed the "*Nitrite figure*." Then the amount of diazonium solution needed is determined, this figure being known as the "*Coupling figure*." If both figures agree we know that the melt has been done correctly, but if the nitrite figure is too high, we may conclude that the melt has been too short, whilst if it is less than the coupling figure the temperature of the melt was too high. A properly prepared aminonaphthol sulphonic acid should give nitrite and coupling figures which agree to within less than 1 per cent.

It is hardly necessary to add that all these estimations, as in all cases of quantitative analysis, should be done in duplicate.

Aminonaphthol disulphonic acid 1:8:3:6: (*H-acid*).

(a) *Nitrite figure* (calculated upon the acid sodium salt, mol. 341): 3·41 gms. H-acid are dissolved in 5 c.cs. of 10 % sodium carbonate solution, diluted to 250 c.cs., precipitated with 25 c.cs. concentrated hydrochloric acid and diazotized at 5° with normal nitrite. The H-acid should give a fine yellow diazo compound which separates in beautiful crystals on salting out. The number of c.cs. used multiplied by 10 gives the percentage.

(b) *Coupling figure:* 3·41 gms. H-acid are dissolved in 50 c.cs. of 10 % sodium carbonate solution, which are then diluted to 300 c.cs., and N/10 diazobenzene solution is then added until a slight excess is present. To test this a little heap of salt is placed upon a piece of filter-paper, and to it is added a few drops of the red solution. After waiting five minutes the colourless rim is touched with the diazotized aniline solution. If H-acid is still present a red rim is at once produced. If diazo solution is in excess a drop of H-acid solution will also give a red rim. The last portions of H-acid often separate out but slowly from the dye so that towards the end it is necessary to wait for a quarter of an hour. At the very end there is always a more or less strong after-coupling. The purer the H-acid the fainter this after-effect. The nitrite figure for a good H-acid is about 0·3 % higher than the coupling figure. The number of c.cs. of aniline solution used gives the percentage composition.

All the aminonaphthol disulphonic acids and monosulphonic acids are determined in this way. The diazonium solution is placed in a 100 c.c. measuring cylinder, and the percentage read off directly. Many works use ice-jacketed burettes which are very neat, but somewhat complicated. For stirring, a stirring rod is used, the end of which is bent round in a big loop. The coupling is carried out in a clean porcelain dish.

Estimation of Naphthol Sulphonic Acids, Disulphonic Acids, and of Dihydroxy Naphthalene Mono- and Di-Sulphonic Acids.

Example: Neville and Winther's Acid (=*Naphthol sulphonic acid* 1:4). *M.w.* 224.

The acid is coupled with N/10 aniline solution exactly as described for H-acid, the dye being salted out in the dish towards the end of the reaction so that it becomes easy to determine the remainder of the acid. Using 2·24 gms. of the acid the number of c.cs. of aniline solution used up gives directly the percentage of H-acid. The coupling is effected at 0°.

Schäffer-salt, R-salt, and other naphthol sulphonic acids are also estimated in the same way. Sultones, however, must first be hydrolysed by treatment with a little hot caustic soda.

Dihydroxynaphthalene mono- and di-sulphonic acids couple up so rapidly, even as regards the second coupling, that the reaction is effected in acetic acid solution in presence of sodium acetate, by means of aniline or the more energetic *p*-aminoacetanilide. In many cases the coupling takes several hours, *e.g.* with dihydroxynaphthalene disulphonic acid 1:8:3:6 (chromotrope acid), and, in addition, the resultant colouring matter separates out from the unchanged chromotrope acid only slowly owing to its great solubility, so that great care must be taken.

It is sometimes possible to estimate various sulphonic acids in presence of one another, but the results obtained are rarely accurate.

For instance, Schäffer salt (sodium naphthol sulphonate 2:6) can be determined fairly accurately in presence of R-salt (sodium naphthol disulphonate 2:3:6) in the following manner: first of all the total amount of material capable of being coupled up is estimated with "aniline solution." Another portion is then dissolved in as small a quantity of water as possible, and to it is then added twenty times its volume of 96 % alcohol. The R-salt is precipitated and the residue can be analysed for its Schäffer content whilst the disulphonic acid can be estimated in the extract. It is necessary to shake up the precipitate with the alcohol (after mixing) for half an hour as otherwise too much Schäffer salt is occluded.

An alternative method consists in first estimating the total by means of aniline solution and then removing the Schäffer salt from a second portion by means of formaldehyde. For example, 5 gms. of the mixture are dissolved in 100 c.cs. water, 5 c.cs. pure 30 % hydrochloric acid are added and 2·5 c.cs. 40 % formaldehyde, and the mixture heated on the water-bath for an hour, after which the disulphonic acid is determined. The difference between the two figures gives the content of mono-sulphonic acid.

Yet a third method may be noted, the Iodine method, which depends upon the following fact. Iodine reacts with R-salt, and also with Schäffer salt, preferably in the presence of sodium bicarbonate. The mixture is first titrated directly with N/10 iodine solution, using an excess of this, and then titrating back. Another sample is then separated by means of alcohol, as noted above, and the extract titrated again. This method is believed by the Elberfeld works to be the best, as the coupling method gives too high results, and so far as can be ascertained this contention appears to be correct.

Test Papers.

(1) *Red and blue Litmus paper.*—This is used as an indicator for all weak and strong bases and acids. It is turned red by acids and blue by alkalis.

Preparation: Best quality litmus should be used. The cubes, containing 50–90 % of calcium sulphate, are ground up and extracted once each with benzene and with alcohol. 4 or 5 Gms. of the substance are then dissolved in a litre of water, and pure filter-paper is soaked in the solution.

To dry the paper it is hung up on threads, and the sheets are then cut up into strips. For red litmus paper a few drops of acetic acid are added to the solution, whilst ammonia is used for the blue paper. The less pronounced the coloration of the paper the more sensitive it is.

(2) *Congo Paper.*—Used for strong acids. It is rendered a pure blue by mineral acids and violet by strong organic acids.

Preparation: 0·5 gms. concentrated Congo Red are dissolved in a litre of water and 5 drops acetic acid are added. Filter-paper is soaked in the warm solution and allowed to dry in a clean place.

(3) *Thiazole Paper* (Mimosa Paper).—Used for free alkali. It is coloured a pure red by alkalis, and is much preferable to Turmeric. It is prepared in the same way as Congo paper, except that the acetic acid is omitted. Ammonia is without influence upon this paper even in high concentrations.

(4) *Phenolphthalein Paper.*—It is turned red by alkalis. It reacts with ammonia and with sodium carbonate, but not with bicarbonates. It may be used with advantage for the more accurate types of analysis.

Preparation: 1 gm. Phenolphthaleïn is dissolved in 1 litre of hot water, and filter-paper is soaked in the hot solution.

(5) *Starch Iodide Paper* (Nitrite Paper).—Used for nitrous acid and for hypochlorites. It becomes bluish-violet with a trace of oxidizing agent, and deep brown with excess. Care must be taken that the paper is merely touched with the drop of solution and that the glass rod is not scraped across it.

Preparation: 10 gms. of pure starch are ground up with a little water and the paste is then poured into a litre of boiling water with good stirring. After cooling, 2 gms. potassium iodide are added, and pure filter-paper is soaked in it and allowed to dry in a clean atmosphere. This paper will indicate clearly in a 1 % hydrochloric acid the addition of a single drop of normal nitrite per litre; it is thus extremely sensitive.

(6) *Lead Paper.*—Used for detecting hydrogen sulphide.

Preparation: Filter-paper is soaked in a solution of 5 gms. lead nitrate per litre, and is then dried in an atmosphere free from sulphuretted hydrogen. Instead of this paper one may use paper soaked in a solution either of ferrous sulphate or of lead acetate.

Solutions of Reagents used for "Spotting" on Filter-Paper.

(1) *H-acid solution.*—1 %, with 5 % sodium carbonate. This solution is used to indicate the presence of easily coupling diazo compounds in the rim of spots on filter-paper. In place of H-acid, R-salt, β-naphthol, hydrocyanic acid, etc., may be used.

(2) *Resorcinol solution.*—1 %, with 5 % sodium carbonate. This is used for detecting any diazo compound, even those which do not react with H-acid (*e.g.* Aminonaphthol sulphonic acid 1:2:4).

(3) *Diazotized* p-*Nitraniline*.—This reacts with phenols and with amines. It must be preserved in the dark and will give a yellow coloration with sodium carbonate alone after 1–2 days, so that care must be taken in its use. *o*-Chloraniline may be used equally well in place of *p*-Nitraniline.

(4) *Alkali sulphide solution.*—For detecting heavy metals in solution such as Iron, Copper, Tin, etc.

Evaluation of Zinc Dust.

1 Gm. of zinc dust and 4·00 gms. sodium bichromate are dissolved up, and the solution made up to a litre with the addition of 20 c.cs. of 20 % sulphuric acid.

250 C.cs. of this solution are taken and diluted up with 900 c.cs. water. 150 C.cs. of 20 % sulphuric acid are added and 100 c.cs. of 10 % potassium iodide. This solution is allowed to stand *in the dark* for half an hour and the excess of iodine titrated back with N/10 thiosulphate.

In order to determine the strength of the bichromate exactly 0·800 gm. is treated in a similar manner.

Calculation : If B = c.cs. thiosulphate for 0·800 gm. bichromate,
A = c.cs. for 4 gms. bichromate plus zinc dust,
then % metallic zinc = $(B \times 1{\cdot}25 - A) \times 1{\cdot}308$.

Evaluation of Lead Peroxide Paste.

About 3–5 gms. of a good average sample of the paste is weighed out accurately between two watch glasses. 5 Gms. of Mohr's salt is then added, and the whole rinsed into a 200 c.c. flask. The mixture is then heated up on a boiling water-bath for half an hour and 25 c.cs. concentrated sulphuric acid are added.

It is boiled up once, and, after cooling, the excess of Mohr's salt is titrated back by means of potassium permanganate.

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